

**Effect of composition and stereoregularity on phase-transition behavior of aqueous
N-ethylacrylamide/*N*-*n*-propylacrylamide copolymer solutions**

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Abstract

Radical copolymerizations of *N*-ethylacrylamide and *N*-*n*-propylacrylamide (NNPAAm) at various ratios were carried out at -40°C, in toluene in the presence of 3-methyl-3-pentanol, or in *N*-ethylacetamide. Syndiotactic-rich copolymers with *racemo* diad contents of 67.1–70.2%, and isotactic-rich copolymers with *meso* diad contents of 60.9–64.5% were prepared. Syndiotactic-rich copolymers with NNPAAm compositions of ≥ 92.9 mol% exhibited large hystereses in the phase-transition temperatures of their aqueous solutions. Isotactic-rich copolymers with NNPAAm compositions of 39.2–67.6 mol% exhibited large hystereses in the phase-transition temperatures of their aqueous solutions. Those of composition > 67.6 mol% were insoluble in water. Stereosequence analysis suggested that isotactic sequences favored intramolecular hydrogen bonding between contiguous NNPAAm units, more than syndiotactic sequences. Enhanced intramolecular hydrogen bonding in isotactic sequences was responsible for the large hystereses and insolubility of isotactic-rich copolymers with high NNPAAm compositions.

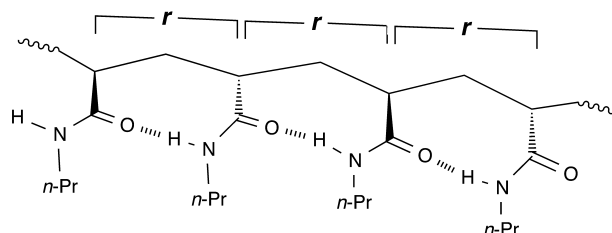
Keywords: Stereoregular *N*-alkylacrylamide copolymers; Chemical composition; Phase-transition behavior

1. Introduction

Poly(*N*-isopropylacrylamide) [poly(NIPAAm)] has been extensively studied as a temperature-sensitive polymer [1-3]. Aqueous poly(NIPAAm) solutions exhibit a soluble-insoluble (or coil-globule) transition at ca. 32°C. This transition occurs rapidly and reversibly upon temperature change. Stereoregularity refers to the consistency in stereochemistry of repeating units in polymers, and that of poly(NIPAAm) significantly influences its phase-transition behavior. For example, an increase in *racemo* (*r*) diad (two contiguous structural units in opposing orientation) content sharpens phase transition at slightly higher temperatures and reduces hysteresis (i.e., retardation observed upon cooling) [4, 5].

Poly(*N*-*n*-propylacrylamide) [poly(NNPAAm)] contains straight propyl groups as *N*-substituents (instead of isopropyl groups), and also exhibits temperature-responsive behavior [6-9]. An increase in the *r* diad content of poly(NNPAAm) sharpens phase transition at slightly higher temperatures during heating, but results in a significantly enlarged hysteresis. This is because of the unusual decrease in phase-transition temperature during cooling [10]. Thus, the phase-transition behavior of aqueous poly(*N*-alkylacrylamide)s depends on both *N*-substituents and stereochemistry.

We previously investigated the effects of chemical composition and stereoregularity of poly(NIPAAm-*co*-NNPAAm)s on the phase-transition behavior of their aqueous solutions [11]. A large hysteresis was only observed when the average length of *r* diads of contiguous NNPAAm units (\bar{n}_{r-N}) was ≥ 2.81 . The IR amide I fraction from intra/intermolecular hydrogen-bound C=O was larger for *r* diad-rich poly(NNPAAm) than atactic (random stereochemistry sequence) poly(NNPAAm), at above the phase-transition temperature [12]. Intramolecular hydrogen bonding between amide groups in contiguous NNPAAm units in syndiotactic arrangement in the dehydrated state was thought to be responsible for the large hysteresis (Scheme 1).



Scheme. 1 Proposed intramolecular hydrogen bonding between amide groups in contiguous NNPAAm units, in syndiotactic arrangement in the dehydrated state.

Increased *meso* (*m*) diad (two adjacent structural units in identical orientation) content has been found to decrease the phase-transition temperature of aqueous poly(*N*-alkylacrylamide)s [5, 13-15]. Consequently, *m*-diad-rich poly(NIPAAm) and

poly(NNPAAm) become insoluble in water, even at lower temperatures. To the best of our knowledge, molecular-level mechanistic information on the phase-transition behavior of *m* diad-rich poly(*N*-alkylacrylamide)s has been little explored, except for oligomer-level details [16, 17].

Poly(*N*-ethylacrylamide) [poly(NEAAm)] also exhibits phase-transition behavior in water, and its phase-transition temperature is much higher than those of poly(NIPAAm) and poly(NNPAAm) [6, 18, 19]. Introducing NEAAm in isotactic *N*-alkylacrylamide (co)polymers should yield more detailed information on phase-transition behavior. Herein, stereoregular poly(NEAAm-*co*-NNPAAm)s were prepared by stereospecific low-temperature radical polymerizations. The effect of *m* diad content on phase-transition behavior was investigated by monitoring changes in hysteresis. Contiguous NNPAAm units in isotactic sequence was found to favor intramolecular hydrogen bonding more than those in syndiotactic sequence. This would be responsible for decrease in phase-transition temperature of aqueous isotactic-rich *N*-alkylacrylamide (co)polymers.

2. Experimental

2.1. Materials

NEAAm and NNPAAm were prepared as previously reported [10, 19]. Dimethyl 2,2'-azobisisobutyrate (MAIB) (Otsuka Chemical, Osaka, Japan) was recrystallized from methanol. Toluene (Kanto Chemical, Tokyo, Japan) was purified by washing with sulfuric acid, water, and 5% aqueous NaOH, followed by fractional distillation. Acetonitrile (Kanto Chemical), 3-methyl-3-pentanol (3Me3PenOH), and *N*-ethylacetamide (Tokyo Chemical Industry, Tokyo, Japan) were used as received.

2.2. Copolymerization

A typical copolymerization procedure was as follows. NEAAm (0.1239 g, 1.26 mmol), NNPAAm (0.1414 g, 1.26 mmol), and MAIB (0.0058 g, 2.52×10^{-2} mmol) were diluted with *N*-ethylacetamide to a total volume of 5 mL, 4 mL of which was transferred to a glass ampoule, cooled to -40°C , degassed, and filled with nitrogen six times. The mixture was irradiated at a distance of ca. 5 cm by an UV-LED lamp (375 nm, Optocode Co., Tokyo, Japan) to initiate photocopolymerization. After 4 h, the reaction mixture was poured into diethyl ether (300 mL). The copolymer precipitate was collected by filtration or centrifugation and dried *in vacuo*. The copolymer yield was determined gravimetrically.

2.3. Measurements

400 MHz ^1H NMR spectra and 100 MHz ^{13}C NMR spectra were obtained using an ECX-400 spectrometer (JEOL, Tokyo, Japan). The diad tacticity of copolymers was determined from the ^1H NMR signals. Signals from main chain methine groups and in-chain methylene groups with *m* configuration at a lower magnetic field were used (deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) at 150°C). This was because the signal from side chain methylene groups in NNPA_m units overlapped with those of in-chain methylene groups with *r* configuration, and with another from those with *m* configuration, at a higher magnetic field [20]. The triad tacticity of copolymers was determined from ^{13}C NMR signals of main chain methine groups in a mixed solvent ($\text{DMSO-}d_6$: D_2O : 2,2,3,3,4,4,5,5-octafluoro-1-pentanol at 75: 10: 15 wt%) at 100°C [5].

Molecular weights and molecular weight distributions of copolymers were determined by size exclusion chromatography (SEC), using polystyrene samples as molecular weight standards. SEC was performed with an HLC 8220 chromatograph (Tosoh, Tokyo, Japan), equipped with TSK gel columns (SuperHM-M (6.5 mm ID \times 150 mm) and SuperHM-H (6.5 mm ID \times 150 mm)) (Tosoh). Dimethylformamide containing LiBr (10 mmol/L) was used as the eluent at 40°C , at a flow rate 0.35 mL/min. The initial polymer concentration was 1.0 mg/mL.

The transmittance of aqueous copolymer solutions (0.1 w/v%) was monitored

at 500 nm as a function of temperature, using a UV/VIS spectrophotometer (V-550, JASCO, Tokyo, Japan) equipped with a Peltier thermostat-controlled single-cell holder (ETC-505, JASCO). The temperature was increased from 2 to 70°C, at a rate of 0.5°C/min, held at 70°C for ca. 15 min, then decreased to 2°C at a rate of 0.5°C/min. The initial temperature was changed to 22°C for measurements of poly(NEAAm-*co*-NNPAAm)s with higher NEAAm compositions. The cloud point (T_c) in the heating and cooling processes was taken as the temperature at which the transmittance was 50%. When residual transparency was observed above the phase-transition temperature, T_c was defined as the temperature at which the average transmittance before and after the phase transition was observed.

IR spectra were measured using a FT-IR spectrometer equipped with a TGS detector (FT/IR-620, JASCO). The copolymer was dissolved in D₂O at a concentration of 1.0×10^2 mg/mL. The copolymer solution (10 μ L) was placed between two CaF₂ windows, at a path length of 10 μ m. The IR cell was attached to a metal cell holder, and the temperature was controlled using a circulating water bath. D₂O was used as the solvent to avoid the overlap of amide I and H₂O O-H bending bands [9].

Dynamic light scattering (DLS) measurements were carried out with an ALV/CGS-3/7002 goniometer system (ALV, Langen, Germany), consisting of a 22 mW

He-Ne laser with a wavelength of 632.8 nm (Model 1145P, JDS Uniphase), multiple τ digital real-time correlator (ALV-7002/Digital Correlator, ALV), and an avalanche photodiode (ALV/High QE APD, ALV). All measurements were performed at 15 and 45°C. The intensity of scattered light was measured at a fixed scattering angle of 90°. The intensity correlation function obtained from the DLS measurement was analyzed using attached software, to obtain the distribution of hydrodynamic radius R_H .

3. Results and Discussion

3.1. Stereoregular poly(NEAAm)s: synthesis and aqueous phase-transition behavior

We previously reported that the *N*-substituent in *N*-alkylacrylamides influenced the stereospecificity of their radical polymerization [10, 20]. The induced stereospecificity when polymerizing *N*-methylacrylamide was smaller than that when using more bulky NIPAAm and NNPAAm. In the current study, the radical polymerization of NEAAm was first conducted under the conditions at which syndiotactic- and isotactic-rich poly(NIPAAm)s were prepared.

Radical polymerization of NEAAm in toluene at -40°C in the presence of 3Me3PenOH afforded syndiotactic-rich poly(NEAAm), with an *r* diad content of 68.3% (Table 1, run 1). This value is comparable to those of poly(NIPAAm) (*r* = 69%) [4] and

poly(NNPAAm) ($r = 70\%$) [10], prepared under corresponding conditions. Radical polymerization of NEAAm in acetonitrile at -40°C afforded a polymer with an m diad content of 54.0% (Table 1, run 2). This value is slightly lower than that of poly(NIPAAm) ($m = 57\%$), prepared under corresponding conditions [21]. NEAAm polymerization was carried out in *N*-ethylacetamide, because radical polymerization of *N*-*n*-propyl- α -fluoroacrylamide in *N*-ethylacetamide afforded a polymer with mm triad content higher than that in acetonitrile [22]. The induced isotactic specificity was slightly enhanced, and a polymer with an m diad content of 63.4% was obtained (Table 1, run 3).

Table 1.

Radical polymerization of NEAAm at -40°C for 4 h, and T_c in the heating and cooling processes of the obtained polymers

Run	Solvent	Added alcohol	Yield %	Tacticity / % ^a		M_n^b 10^{-4}	M_w^b M_n	$T_c / ^{\circ}\text{C}$	
				m	r			heating	cooling
1	Toluene	3Me3PenOH	95	31.7	68.3	8.95	2.6	80.3	80.0
2	Acetonitrile	None	60	54.0	46.0	4.13	4.8	-	-
3	<i>N</i> -Ethylacetamide	None	77	63.4	36.6	7.11	2.0	85.0	84.5
4 ^c	Toluene	3Me3PenOH	75	33.7	66.3	1.84	3.5	>95	>95
5 ^c	<i>N</i> -Ethylacetamide	None	84	62.5	37.5	1.65	2.1	>95	>95

[NEAAm]₀ = 0.5 mol/L, [MAIB]₀ = 0.5×10^{-2} mol/L, [3Me3PenOH]₀ = 2.0 mol/L

^a Determined by ¹H NMR signals

^b Determined by SEC (polystyrene standards)

^c [MAIB]₀ = 0.2×10^{-1} mol/L

Fig. 1a shows the temperature dependence of transmittance for aqueous solutions of poly(NEAAm)s (Table 1, runs 1 and 3). Isotactic-rich poly(NEAAm) exhibited a higher phase-transition temperature than syndiotactic-rich poly(NEAAm), in

both the heating and cooling processes. This trend is opposite to that observed for poly(NIPAAm)s [4, 5] and poly(NNPAAm)s [10]. Poly(NEAAm)s with lower molecular weights (Table 1, runs 4 and 5) exhibited phase-transition temperatures higher than those of poly(NEAAm)s with higher molecular weights (Fig. 1b), regardless of stereoregularities. Phase-transition temperatures of aqueous poly(NEAAm)s have been reported to increase with decreasing molecular weight [23]. In contrast, the molecular weight of poly(NIPAAm) has little effect on phase-transition behavior, at least when $M_w > 5.0 \times 10^4$ [24]. This suggests that molecular weight has a greater effect than stereoregularity on the phase-transition behavior of aqueous poly(NEAAm)s. This is most likely because the phase-transition temperatures of poly(NEAAm)s are much higher than those of poly(NIPAAm)s and poly(NNPAAm)s. In Fig. 1, hysteresis was largely absent, regardless of stereoregularities and molecular weights.

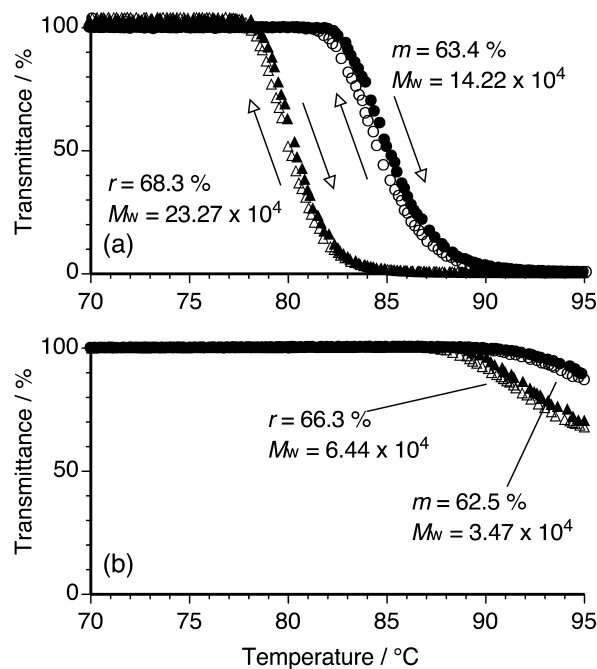


Fig. 1 Effect of stereoregularity and molecular weight on temperature dependence of transmittance, for isotactic-rich (●, ○) and syndiotactic-rich (▲, △) poly(NEAAm)s. (a) Higher and (b) lower molecular weight poly(NEAAm)s (0.1 w/v%, heating/cooling rate = 0.5°C/min).

3.2. Stereoregular poly(NEAAm-co-NNPAAm)s: synthesis and aqueous phase-transition behavior

To decrease the phase-transition temperature, radical copolymerization of NEAAm and NNPAAm was carried out (Tables 2 and 3) at -40°C, in toluene in the presence of 3Me3PenOH, or in *N*-ethylacetamide. NNPAAm was selected as a comonomer to monitor hysteresis changes [11]. Chemical compositions of NEAAm units in the copolymers were comparable to the NEAAm fractions in the feed, regardless of

polymerization conditions. However, copolymerizations were quenched before the monomer had been completely consumed. This suggests the radical copolymerization of NEAAm and NNPAAm proceeded in an almost random manner. Copolymer tacticities were also comparable to each other, regardless of polymer chemical compositions and polymerization conditions. This suggests that the syndiotactic specificity induced by 3Me3PenOH and the isotactic specificity induced in *N*-ethylacetamide were independent of the monomer ratio.

Table 2.

Radical copolymerization of NEAAm and NNPAAm, in toluene at -40°C for 20 min in the presence of 3Me3PenOH, and T_c in the heating and cooling processes of the obtained polymers

Run	NNPAAm / mol%		Yield %	Tacticity / % ^a		\bar{n}_{r-N} ^b	M_n^c 10 ⁻⁴	M_w^c M_n	T_c / °C	
	in feed	in copolymer		<i>m</i>	<i>r</i>				heating	cooling
1 ^d	0.0	0.0	95	31.7	68.3	-	8.95	2.6	80.3	79.9
2	10.2	10.6	49	32.6	67.4	1.08	10.6	2.3	68.4	68.4
3	20.1	20.5	39	32.4	67.6	1.16	14.0	2.2	61.2	61.2
4	30.2	30.0	42	31.7	68.3	1.26	12.2	2.3	55.4	55.3
5	41.0	40.7	47	32.9	67.1	1.38	13.1	2.2	50.0	49.6
6	49.9	49.6	66	31.9	68.1	1.51	11.9	2.3	46.4	46.3
7	55.1	54.7	51	32.5	67.5	1.59	18.4	2.1	44.0	43.8
8	60.0	59.3	53	31.3	68.7	1.69	11.5	2.0	43.1	42.9
9	70.1	69.2	56	32.0	68.0	1.89	11.1	1.6	38.3	38.0
10	79.5	77.6	59	30.2	69.8	2.18	12.8	1.9	34.7	33.5
11	89.9	87.6	63	30.6	69.4	2.55	11.4	3.0	29.9	23.6
12	95.1	92.9	66	30.4	69.6	2.84	15.3	2.0	27.5	12.8
13	100.0	100.0	74	29.8	70.2	3.36	13.9	1.9	25.7	10.2

[NEAAm+NNPAAm]₀ = 0.5 mol/L, [MAIB]₀ = 0.5 × 10⁻² mol/L, [3Me3PenOH]₀ = 2.0 mol/L

^a Determined by ¹H NMR signals

^b Average length of *r* diad of contiguous NNPAAm units

^c Determined by SEC (polystyrene standards)

^d For 4 h

Fig. 2a shows the temperature dependence of transmittance of aqueous syndiotactic-rich poly(NEAAm-*co*-NNPAAm)s, with NNPAAm compositions of 10.6, 49.6, 77.6, 87.6, and 92.9 mol% in the heating process (Table 2, runs 2, 6, 10, 11, and 12).

The phase-transition temperature gradually decreased with increasing NNPAAm composition [11, 25].

Table 3.

Radical copolymerization of NEAAm and NNPAAm in *N*-ethylacetamide at -40°C for 4 h, and T_c in the heating and cooling processes of the obtained polymers

Run	NNPAAm / mol%		Yield %	Diad / % ^a			Triad / % ^b			\bar{n}_{m-N}^c	M_n^d	M_w^d	$T_c / ^\circ\text{C}$	
	in feed	in copolymer		<i>m</i>	<i>mm</i>	<i>mr</i>	<i>rr</i>	10^{-4}	M_n		heating	cooling		
1	0.0	0.0	77	63.4	-	-	-	-	7.11	2.0	85.0	84.5		
2	10.8	10.9	51	64.5	47.1	31.6	21.3	1.09	9.84	1.6	75.3	75.1		
3	21.7	21.0	60	63.4	47.4	31.8	20.8	1.19	9.23	1.8	65.7	65.3		
4	30.1	29.1	67	63.8	46.0	31.1	22.9	1.28	9.90	1.7	61.4	59.5		
5	35.0	33.3	48	61.9	49.1	29.6	21.3	1.34	7.62	2.0	58.8	56.3		
6	41.1	39.2	50	62.7	47.5	30.9	21.6	1.42	8.45	2.2	50.4	28.5		
7	45.1	42.9	59	62.7	46.6	32.6	20.8	1.47	9.65	1.9	48.2	25.3		
8	50.9	49.0	58	62.5	46.4	32.8	20.8	1.57	7.75	2.0	46.1	22.4		
9	60.1	57.9	68	62.2	48.0	31.7	20.3	1.77	8.02	2.0	40.2	17.4		
10	69.8	67.6	70	62.5	45.6	31.5	22.9	2.01	7.55	2.1	36.5	12.6		
11	72.1	69.6	75	61.3	-	-	-	-	7.19	2.1	-	-		
12	79.5	76.9	67	61.1	-	-	-	-	8.34	1.9	-	-		
13	89.9	87.2	72	60.9	-	-	-	-	8.30	1.9	-	-		

[NEAAm+NNPAAm]₀ = 0.5 mol/L, [MAIB]₀ = 0.5 × 10⁻² mol/L

^a Determined by ¹H NMR signals

^b Determined by ¹³C NMR signals

^c Average length of *m* diad of contiguous NNPAAm units

^d Determined by SEC (polystyrene standards)

The phase-transition temperature in the cooling processes also gradually decreased with increasing NNPAAm composition, for copolymers with lower NNPAAm compositions (Fig. 2b). The phase-transition behavior of the copolymer with 87.6 mol% NNPAAm composition exhibited a significantly broadened profile (Table 2, run 11), probably because of distributions of stereoregularity and monomer sequencing [11, 26]. A sharp temperature transition profile was exhibited for poly(NEAAm-*co*-NNPAAm) with NNPAAm composition of 92.9 mol%, and was accompanied by a large decrease in the phase-transition temperature. This is consistent with results for poly(NIPAAm-*co*-NNPAAm) [11]. Therefore, it is assumed that intramolecular hydrogen bonding of contiguous NNPAAm units in syndiotactic sequence in the dehydrated state was responsible for the large hysteresis, even though the comonomer was changed from NIPAAm to NEAAm. Some residual transparency was observed above the phase-transition temperature for the copolymer with NNPAAm composition of 77.6 mol%, and is discussed later.

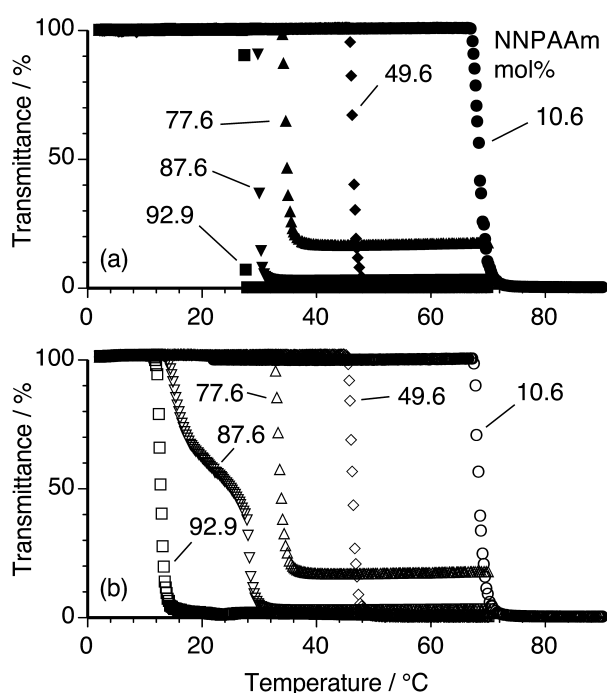


Fig. 2 Effect of chemical composition on temperature dependence of transmittance for syndiotactic-rich poly(NEAAm-*co*-NNPAAm)s. (a) Heating and (b) cooling processes (0.1 w/v%, heating/cooling rate = 0.5°C/min).

Fig. 3a shows the temperature dependence of transmittance of aqueous isotactic-rich poly(NEAAm-*co*-NNPAAm)s, with NNPAAm compositions of 10.9, 29.1, 39.2, and 67.6 mol%, in the heating process (Table 3, runs 2, 4, 6, and 10). The phase-transition temperature gradually decreased, and residual transparency above the phase-transition temperature significantly increased, with increasing NNPAAm composition. Isotactic-rich copolymers with NNPAAm compositions >67.6 mol% were insoluble.

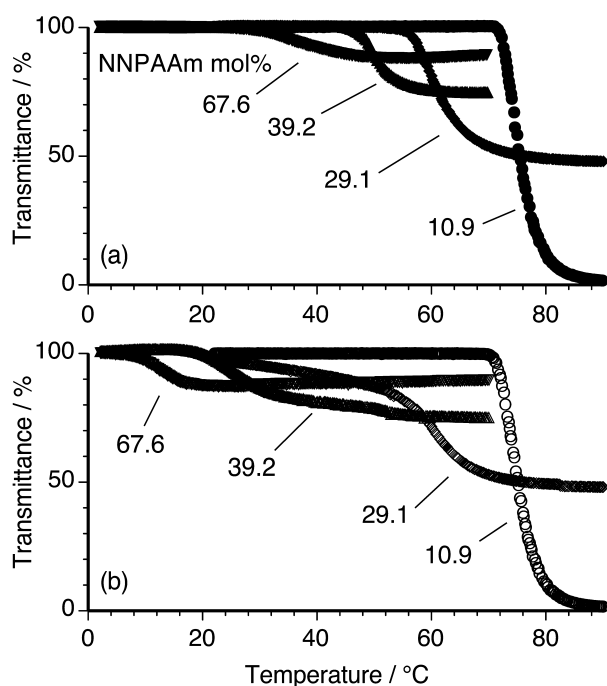


Fig. 3 Effect of chemical composition on temperature dependence of transmittance for isotactic-rich poly(NEAAm-*co*-NNPAAm)s. (a) Heating and (b) cooling processes (0.1 w/v%, heating/cooling rate = 0.5°C/min).

The phase-transition behavior in the cooling process of the copolymer with 29.1 mol% NNPAAm composition was significantly broadened (Fig. 3b). A large decrease in the phase-transition temperature in the cooling process was observed between copolymers with NNPAAm compositions of 33.3 and 39.2 mol% (Table 3, runs 5 and 6). Thus, hysteresis was discontinuously enhanced at a certain NNPAAm fraction in both the isotactic- and syndiotactic-rich copolymer systems.

3.3. Stereosequence analysis

Copolymerizations of NEAAm and NNPAAm proceeded in an almost random manner, and tacticities were independent of monomer ratio. The triad tacticity distribution in syndiotactic-rich poly(NIPAAm), prepared in toluene at -80°C in the presence of ethanol, obeyed Bernoullian statistics [27]. \bar{n}_{r-N} was estimated from triad tacticities (calculated from diad tacticities based on Bernoullian statistics) and chemical compositions for syndiotactic-rich copolymers, according to a previously reported method [11]. The triad tacticity distribution in isotactic-rich poly(NIPAAm) prepared in polar solvents did not obey Bernoullian statistics [28]. The average length of m diad for contiguous NNPAAm units (\bar{n}_{m-N}) in isotactic-rich copolymers was estimated from triad tacticities, which were determined from ^{13}C NMR signals of main-chain methine carbons. Fig. 4 shows the difference in phase-transition temperature between heating and cooling (ΔT_c), plotted against \bar{n}_{r-N} of syndiotactic-rich copolymers or \bar{n}_{m-N} of isotactic-rich copolymers.

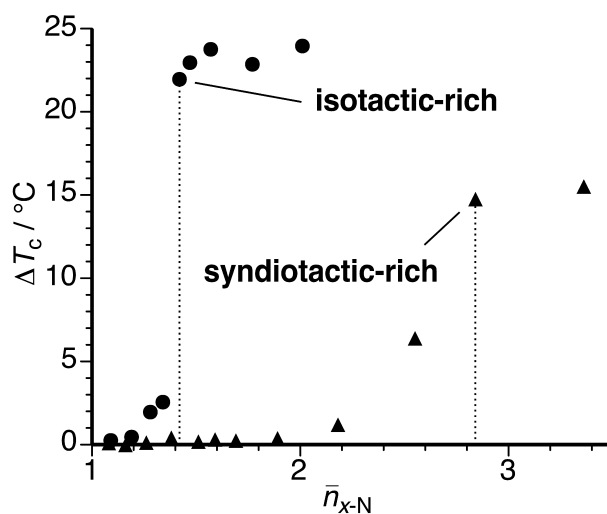


Fig. 4 Relationship between ΔT_c and \bar{n}_{r-N} for isotactic-rich poly(NEAAm-*co*-NNPAAm)s or \bar{n}_{r-N} for syndiotactic-rich poly(NEAAm-*co*-NNPAAm)s.

Only syndiotactic-rich copolymers with $\bar{n}_{r-N} \geq 2.84$ exhibited obvious large hystereses (Table 2, runs 12–13). Syndiotactic-rich copolymers with $\bar{n}_{r-N} \leq 2.18$ exhibited small hystereses (Table 2, runs 2–10). The copolymer with $\bar{n}_{r-N} = 2.55$ exhibited a gradual phase transition during cooling and a moderate hysteresis (Fig 2b and Table 2, run 11). Similar results were observed in the syndiotactic-rich poly(NIPAAm-*co*-NNPAAm) system ($\bar{n}_{r-N} \geq 2.81$), and the critical values for the two systems were comparable. The large hystereses for syndiotactic-rich poly(NIPAAm-*co*-NNPAAm)s are proposed to have originated from enhanced aggregation, by hydrophobic interaction between copolymers in the dehydrated state. Enhanced aggregation would have been facilitated by intramolecular hydrogen bonding between amide groups of adjacent NNPAAm units in

syndiotactic sequence [11]. The formation of intramolecular hydrogen bonding by an average 3.84 NNPAAm monomeric units in syndiotactic sequence is assumed to be responsible.

Isotactic-rich copolymers with $\bar{n}_{m-N} \geq 1.42$ exhibited large hystereses (Table 3, runs 6–10), whereas those of $\bar{n}_{m-N} \leq 1.34$ exhibited small hystereses (Table 3, runs 2–5). If the large hystereses in isotactic-rich copolymers originated via a similar mechanism to that in syndiotactic-rich copolymers, then intramolecular hydrogen bonding by an average 2.42 NNPAAm units in isotactic sequence should be responsible. Isotactic-rich copolymers with NNPAAm compositions >67.6 mol% ($\bar{n}_{m-N} = 2.01$) were insoluble. Thus, isotactic sequencing is assumed to have favored intramolecular hydrogen bonding more than syndiotactic sequencing. This resulted in differing water solubility between the isotactic- and syndiotactic-rich *N*-alkylacrylamide copolymers.

FT-IR measurements revealed the relationship between stereostructure and intramolecular hydrogen bonding. Fig. 5 shows amide I regions of the IR spectra of the syndiotactic- and isotactic-rich copolymers, which are largely composed of the C=O stretching vibration. Symmetric single-mode amide I bands were observed at 18°C, regardless of stereostructure (Fig. 5, left). This suggests that copolymers were soluble in similar hydration states below the phase-transition temperature. Amide I bands became

asymmetric upon elevating the temperature to 47°C (Fig. 5, right). Amide I bands were resolved into two fractions by Gaussian fitting. The intensity of the fraction from intra/intermolecular hydrogen-bound C=O was greater in the isotactic-rich copolymer [29], which is consistent with the above hypothesis.

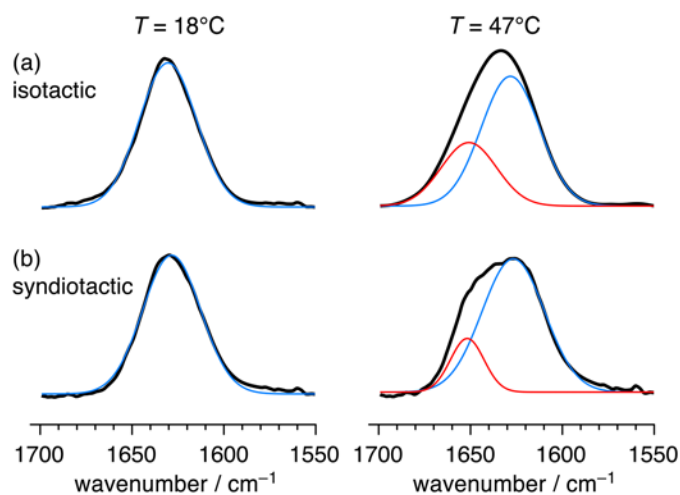


Fig. 5 Baseline-subtracted amide I bands of (a) isotactic-rich poly(NEAAm-*co*-NNPAAm) with NNPAAm composition of 49.0 mol% and (b) syndiotactic-rich poly(NEAAm-*co*-NNPAAm) with NNPAAm composition of 59.3 mol%. Spectra were obtained at (left) below (18°C) and (right) above (47°C) the phase-transition temperature, from best-fitted Gaussian components. Fractions centered at 1627 (blue) and 1651 cm^{-1} (red) resulted from hydrated and intra/intermolecular hydrogen-bound C=O, respectively (polymer concentration = 1.0×10^2 mg/mL).

3.4. Residual transparency above the phase-transition temperature

Fig. 6 shows the relationship between NNPAAm composition in isotactic- and

syndiotactic-rich poly(NEAAm-*co*-NNPAAm)s, and transmittance above the phase-transition temperature. Isotactic-rich copolymers with NNPAAm compositions of 29.1-67.6 mol% exhibited residual high transparency above the phase-transition temperature. Syndiotactic-rich copolymers with NNPAAm compositions of 59.3–77.6 mol% also exhibited some residual transparency. Thus, the stereoregularity and chemical composition significantly affected the transparency above the phase-transition temperature.

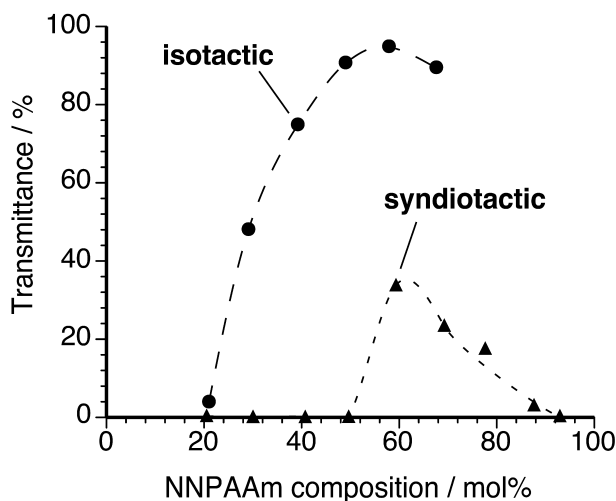


Fig. 6 Relationship between NNPAAM composition in isotactic- or syndiotactic-rich poly(NEAAm-*co*-NNPAAm)s, and transmittance above the phase-transition temperature.

Fig. 7 shows the effect of copolymer concentration or solvent on the temperature dependence of transmittance, for isotactic-rich poly(NEAAm-*co*-NNPAAm)

with NNPAAm composition of 39.2 mol%. Increasing the copolymer concentration from 0.1 to 0.5 wt% slightly lowered the phase-transition temperature, and the solution (0.5 wt%) appeared completely turbid above the phase-transition temperature. This suggests the residual transparency above the phase-transition temperature was due to reduced aggregation of globules. Changing the solvent from H₂O to D₂O slightly increased the phase-transition temperature and significantly reduced the residual transparency, when the copolymer concentration was 0.1 wt%. The increased phase-transition temperature was in accordance with results observed for poly(NIPAAm)s, when the solvent was changed from H₂O to D₂O [30]. The reduced residual transparency suggests that hydrogen bonding plays an important role in this phenomenon, because deuterium bond in D₂O is stronger than hydrogen bond in H₂O [31, 32].

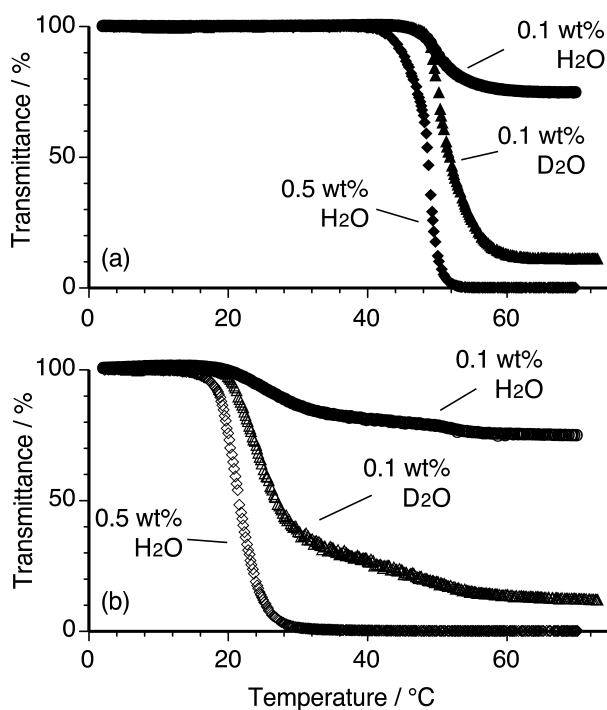


Fig. 7 Effect of copolymer concentration or solvent on temperature dependence of transmittance, for isotactic-rich poly(NEAAm-*co*-NNPAAm) with NNPAAm composition of 39.2 mol%. (a) Heating and (b) cooling processes (heating/cooling rate = 0.5°C/min).

Fig. 8 shows ^1H NMR spectra of the isotactic-rich copolymer with NNPAAm composition of 49.0%, and the syndiotactic-rich copolymer with NNPAAm composition of 49.6%, in D_2O at 25°C. The signals of the former were broadened compared with those of the latter. Splitting from spin-spin coupling was observed in side chain signals of the syndiotactic-rich copolymer, but not in those of the isotactic-rich copolymer. Chain flexibility of the isotactic-rich copolymer was reduced, even below the phase-transition

temperature.

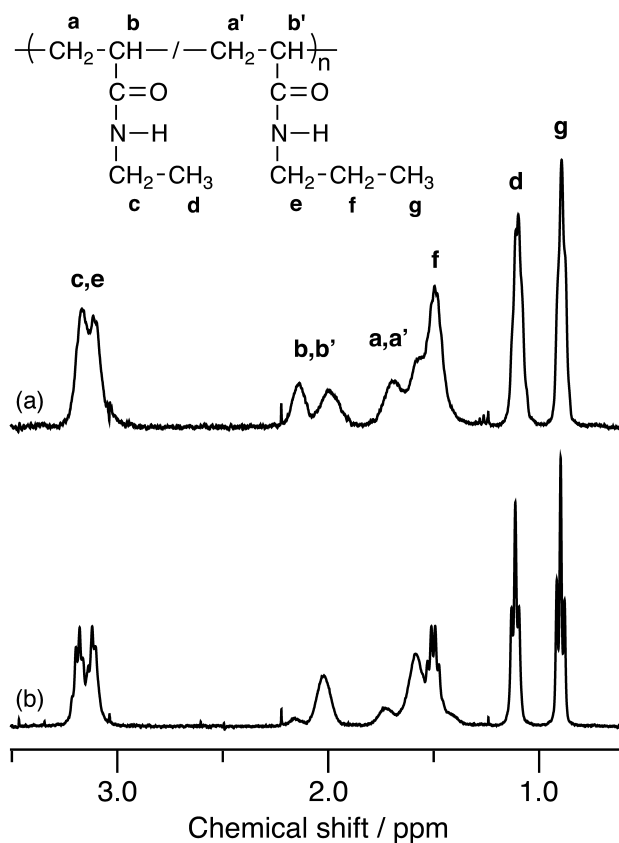


Fig. 8 ¹H NMR spectra of (a) isotactic-rich poly(NEAAm-*co*-NNPAAm) with NNPAAm composition of 49.0 mol% and (b) syndiotactic-rich poly(NEAAm-*co*-NNPAAm) with NNPAAm composition of 49.6 mol%, in D₂O at 25°C (0.1 wt%).

DLS measurements were conducted at 15 and 45°C for the aqueous isotactic-rich copolymer with NNPAAm composition of 67.6 mol%. Residual high transparency was exhibited above the phase-transition temperature (Fig. 3). DLS measurements were also conducted for the aqueous syndiotactic-rich copolymer with NNPAAm composition

of 92.9 mol%. Complete turbidity was exhibited above the phase-transition temperature (Fig. 2). The peak at R_H of 15 nm in the profile of the aqueous syndiotactic-rich copolymer at 15°C was assigned to a single copolymer chain (Fig. 9b left). A larger R_H was observed for the isotactic-rich copolymer at 15°C, although aqueous solutions were filtered with a 0.2- μm syringe filter prior to measurement (Fig. 9a, left). This suggested that the isotactic-rich copolymer did not significantly exist as a single copolymer chain.

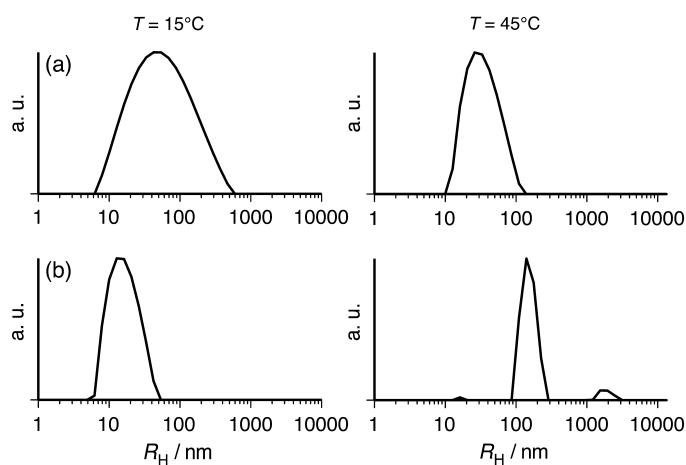


Fig. 9 DLS spectra of (a) isotactic-rich poly(NEAAm-*co*-NNPAAm) with NNPAAm composition of 67.6 mol% and (b) syndiotactic-rich poly(NEAAm-*co*-NNPAAm) with NNPAAm composition of 92.9 mol%, in H₂O at (left) 15 and (right) 45°C (0.1 wt%).

Block copolymers of hydrophilic blocks have been reported to form loose associates in aqueous solution. For example, poly(ethylene oxide)-*block*-poly(NIPAAm) exhibits this behavior at below the poly(NIPAAm) phase-transition temperature [33, 34].

Poly(ethylene oxide)-block-poly(*N,N*-dimethylacrylamide) also does so, and its association behavior differs regarding concentration and block ratio dependences and temperature effects, when compared with micellization in selective solvents [35]. The major driving force for association is considered to be incompatibility between the two blocks, because of their differing interaction with water [35].

A theoretical study of chain conformations of vinyl polymers indicated that the conformational entropy of isotactic chains was lower than that of syndiotactic analogs [36]. In other words, isotactic chain mobility was lower than that of syndiotactic analogs. This lower mobility is expected to enhance the incompatibility with water between the NEAAm and NNPAAm units in isotactic copolymers. Isotactic-rich copolymers with high NNPAAm compositions are insoluble, whereas syndiotactic-rich ones are soluble. Isotactic copolymers should favorably form loose associates, although copolymers in the current study are random copolymers (not block copolymers). The favorable formation of loose associates of the isotactic-rich copolymer was probably the reason for the broadened NMR signals and the larger R_H .

Isotactic- and syndiotactic-rich copolymers exhibited different DLS profiles above the phase-transition temperature. Aggregates with $R_H > 1000$ nm were observed for the aqueous syndiotactic-rich copolymer (Fig. 9b, right). Large aggregates would

significantly decrease the transparency above the phase-transition temperature.

A smaller R_H was observed for the isotactic-rich copolymer above the phase-transition temperature (Fig. 9a, right). The hydrodynamic diameter was estimated to be shorter than the wavelength of visible light, accounting for the high transparency above the phase-transition temperature.

R_H at 45°C was $<R_H$ at 15°C in the case of the isotactic-rich copolymer. The apparent globule concentration above the phase-transition temperature would reduce upon forming loose associates, and more hydrophilic NEAAm units would surround these associates. Globule aggregation would be suppressed, and residual transparency of isotactic-rich copolymers would be enhanced above the phase-transition temperature.

4. Conclusions

The effect of stereoregularity and chemical composition of poly(NEAAm-*co*-NNPAAm)s on the phase-transition behavior of their aqueous solutions was investigated. Only syndiotactic-rich copolymers with \bar{n}_{r-N} values ≥ 2.84 exhibited large hystereses. The \bar{n}_{r-N} value corresponded with that observed for syndiotactic-rich poly(NIPAAm-*co*-NNPAAm) [11]. The hysteresis in the phase-transition behavior of syndiotactic *N*-alkylacrylamide copolymers was explained by intramolecular hydrogen bonding of

contiguous NNPAAm units in syndiotactic sequence in the dehydrated state.

Molecular-level mechanistic information on the phase-transition behavior of isotactic *N*-alkylacrylamide copolymers was similarly obtained, when hydrophilic NEAAm was introduced as a further component. Isotactic-rich copolymers with $\bar{n}_{m-N} = 1.42\text{--}2.01$ exhibited large hystereses. Assuming this originated via a similar mechanism to that in syndiotactic-rich copolymers, intramolecular hydrogen bonding by an average $2.42\text{--}3.01$ NNPAAm units was responsible. Isotactic-rich copolymers with $\bar{n}_{m-N} > 2.01$ were insoluble. This suggested that intramolecular hydrogen bonding by an average > 3.01 NNPAAm units in isotactic sequence was responsible.

Contiguous NNPAAm units in isotactic sequence favored intramolecular hydrogen bonding more than those in syndiotactic sequence. This resulted in differing phase-transition behavior between aqueous isotactic- and syndiotactic-rich *N*-alkylacrylamide (co)polymers.

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