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Polymerization of Acrylamide in Aqueous Solution of Poly(*N*-isopropylacrylamide) at Lower Critical Solution Temperature

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Acrylamide (AAm) was found to polymerize in a solution of poly(*N*-isopropylacrylamide) (PNIPAAm) in water at around its lower critical solution temperature (LCST) (32°C) without any initiators. This phenomenon was specifically observed in aqueous solutions of the polymers having LCST such as PNIPAAm and poly(methylvinylether) (PMVE). AAm polymerized only when PNIPAAm and AAm were dissolved in water below LCST of PNIPAAm and then the solution was warmed up to the polymerization temperature (40°C). On the other hand, the polymerization of AAm did not proceed when AAm was added into aqueous PNIPAAm solution during and after the phase separation above 32°C. Furthermore the polymerizability of AAm was remarkably affected by the concentration and molecular weight of the PNIPAAm additives. Under the condition of lower PNIPAAm concentration (0.30 mol/L), the increase in the molecular weight of PNIPAAm considerably increased the molecular weight of the resulting PAAm but decreased the yield of PAAm. Under the condition of higher PNIPAAm concentration (0.60 mol/L) the polymerizability was not so affected by the molecular weight of PNIPAAm, while the molecular weight of PAAm formed by using higher molecular weight PNIPAAm was higher than those of PAAm formed by using lower molecular weight PNIPAAm. Moreover, the molecular weight of PAAm formed by the PNIPAAm induced polymerization of AAm was much higher than that of the polymer obtained by the radical polymerization using AIBN in THF or VA- 061 in water.

Keywords: poly(*N*-isopropylacrylamide); lower critical solution temperature; acrylamide; water solvent; radical polymerization

1 Introduction

Polyacrylamide (PAAm) is a typical water-soluble polymer, and of great importance and interest from the scientific and practical viewpoints. For example, PAAm is used as flocculating agents for waste water purification, concentration and extraction of metals, reductants of hydrodynamic resistance, and also the structure of soils. In the medical and biological fields, they are widely applied as plasma substitutes for stabilization and purification of some ferment, and for the controlled release of drugs (1–3). Because of the usability of the polymer, the polymerization behavior of acrylamide (AAm) monomer has also attracted a great interest.

In our continuous study of the polymerization of AAm, we have already found that the polymerization of AAm was induced by the poly(methyl vinyl ketone) having carbonyl groups in its side chain as a template polymer, or low molecular weight ketones, without any conventional initiators (4–8). In these polymerization systems, the interaction between the carbonyl oxygen in the additive carbonyl compound and the amide group in the AAm monomer seems to play an important role in the initiation and propagation steps. It has been reported that some types of active methylene containing compounds such as aldehyde and ketones induced the radical polymerization of polar vinyl monomers (9–11). For instance, the polymerization of methyl methacrylate (MMA) was induced by cyclohexanone, and its mechanism was proposed to involve the hydrogen radical transfer from ketone to MMA (12, 13). The detail of the polymerization mechanism, however, has not been clarified yet.

More recently we have investigated the solvent effect on the polymerization of AAm in the presence of the amide groups containing polymers such as poly(*N*-isopropylacrylamide) (PNIPAAm) as template polymers. In particular, water was chosen as a solvent although water must inhibit

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the intermolecular interaction between the amide group of AAm and the amide groups of the template polymers. During the experiments to observe the temperature effects in this polymerization system, we have recently found that the lower critical solution temperature (LCST) of the template polymers concerns the polymerizability of AAm. Namely, AAm was found to polymerize in a solution of PNIPAAm in water at around its LCST (32°C) without any initiators. This phenomenon was specifically observed in aqueous solutions of the polymers having lower critical solution temperature (LCST). It is well-known that aqueous solutions of PNIPAAm undergo phase separation upon raising the temperature beyond about 32°C induced by the hydrophobic interaction (14–16), and this phase behavior of the solutions with hydrophobic bonding and the hydrophilic interaction between the amide groups seem to have a relation with the promotion of the polymerization of AAm. In this study, we have reported this unique polymerization system of AAm in the aqueous solutions of aqueous solutions of the polymers having LCST, such as PNIPAAm, giving important information about the effects of polymerization temperature, concentration, and molecular weights of PNIPAAm on the polymerizability of AAm.

2 Experimental

2.1 General

IR spectra were obtained on a Jasco FT-IR-470 Plus spectrometer. ^{1}H-NMR spectra were measured on a Varian OXFORD NMR300 (300 MHz) spectrometer and the chemical shift values (δ) were expressed in ppm downfield from the internal TMS standard. The molecular weights of PNIPAAm were determined by using a gel permeation chromatography (GPC). The GPC analyses were carried out on a Hitachi L-6000 high performance liquid chromatograph, L-3350 RI detector, and Shodex® GPC KF-804L column. Tetrahydrofuran was used as the eluent with a flow rate of 1.0 mL/min, and molecular weight values were relative to the polystyrene standards (Shodex® STANDARD (SM-105) polystyrene). The molecular weights ($\bar{M}$n) of PAAm were estimated by using the Mark-Houwink equation, $[\eta] = 6.5 \times 10^{-3} \times \bar{M}\text{n}^{0.82}$ (17). Intrinsic viscosities $[\eta]$ were determined by the standard technique using an Ostwald type viscometer in water bath thermostated at 30 ± 0.05°C.

2.2 Materials

Acrylamide (AAm) and *N*-isopropylacrylamide (NIPAAm) (Wako Pure Chemical Industries, Ltd.) were purified by recrystallization from benzene and hexane-benzene (95:5), respectively. 2,2′-Azobisisobutyronitrile (AIBN) and 2,2′-azobis[2-(2-imidazolin-2-yl)propane] (VA-061) (Wako Pure Chemical Industries, Ltd.) as radical initiators were recrystallized from methanol at or below 40°C. Tetrahydrofuran (THF) (Wako Pure Chemical Industries, Ltd.) was distilled from Na-benzophenoneketyl under an argon atmosphere. Pure water for the polymerization solvent was prepared by purification of distilled water (Wako Pure Chemical Industries, Ltd.) using the Simplicity Personal Ultrapure Water System SIMS 700 0J (Millipore Co. Ltd.). Other solvents for recrystallization and reprecipitation such as hexane, benzene, acetone, and diethylether were used without further purification.

2.3 Preparation of Poly(N-isopropylacrylamide) (PNIPAAm)

NIPAAm (300–600 mmol), AIBN (3 mmol), and 150 mL of THF were placed in a glass ampoule under Ar atmosphere. The ampoule was degassed repeatedly by freeze-evacuation-thaw cycles, and sealed *in vacuo*. NIPAAm was then polymerized under light exclusion condition at 40°C for 18 h. After cooling the ampoule in an ice-water bath, the polymer solution was poured into a large amount of diethyl ether, and the resulting precipitate was filtered and dried to constant weight under reduced pressure at room temperature. The crude polymer was purified by reprecipitation from acetone into diethylether.

2.4 Poly(N-isopropylacrylamide)

IR (KBr) 3300, 1649, 1541 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.86–1.21 (m, N-CH(C$\boldsymbol{H}_3$)$_2$), 1.21–1.89 (m, C$\boldsymbol{H}_2$ in main chain), 1.89–2.38 (m, C$\boldsymbol{H}$ in main chain), 3.16–3.28 (br, N$\boldsymbol{H}$), 3.89–4.12 (m, N-C$\boldsymbol{H}$(CH$_3$)$_2$).

2.5 Typical Procedure of the Polymerization of Acrylamide (AAm) in the Presence of PNIPAAm

Acrylamide (6.0 mmol) and PNIPAAm (6.0 mmol based on the amount of the monomer units) were placed in a glass ampoule and dried *in vacuo*. Pure water was added into the ampoule under an argon atmosphere until the total volume reached 20 mL. The ampoule was degassed repeatedly by freeze-evacuation-thaw cycles, and sealed under an argon atmosphere. The resulting clear homogeneous solution was warmed up to the polymerization temperature (40°C). The increase of the turbidity of the solution was observed above 30°C. The polymerization was carried out under light exclusion condition in a water bath thermostated at 40°C for 40 h. After cooling the ampoule in an ice-water bath, the polymer solution was poured into a large amount of acetone, and the resulting precipitate was filtered and dried to constant weight under reduced pressure at room temperature. The crude polymer was purified by reprecipitation from water into acetone.

2.6 Poly(acrylamide)

IR (KBr) 3420, 3198, 1653, 1616 cm^{-1}; ^{1}H-NMR (D_2O) δ 1.21–1.76 (m, C$\boldsymbol{H}_2$), 1.92–2.21 (m, C$\boldsymbol{H}$).

3 Results and Discussion

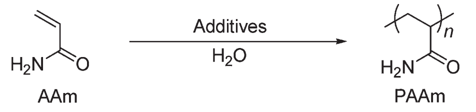
3.1 Polymerization of Acrylamide in a Cloud Solution of Poly(N-isopropylacrylamide) in Water at Lower Critical Solution Temperature

Acrylamide (AAm) was found to polymerize in a solution of poly(*N*-isopropylacrylamide) (PNIPAAm) in water at 40°C without any initiators (Scheme 1, Table 1, entry 2). It was confirmed that thermal polymerizations of AAm were not observed without PNIPAAm in water at 40°C or higher temperature (Table 1, entry 1). This phenomenon was specifically observed in aqueous solutions of the polymers having lower critical solution temperature (LCST). In fact, poly(vinylmethylether) (PVME), which also had a LCST at 37°C (18), induced the polymerization of AAm (Table 1, entry 3). On the other hand, AAm did not polymerize in solutions of other water-soluble polymers such as poly(*N*-vinylacetamide) (PNVA) and poly(*N*-hydroxymethylacrylamide) (NHMAAm) (Table 1, entries 4, 5). *N*-Methylacrylamide, a monomeric *N*-alkylated amide was also ineffective to promote the polymerization (Table 1, entry 6).

3.2 Temperature Dependence of the Polymerization of Acrylamide Induced by Poly(N-isopropylacrylamide)

The temperature dependence of the polymerization of AAm induced by PNIPAAm was remarkable and had a strong relation to LCST of the aqueous solution of PNIPAAm. The polymerization of AAm proceeded above 30°C (Table 2, entry 2) and the yield of polyacrylamide (PAAm) showed a maximum at about 50°C (Table 2, entry 4). A higher polymerization temperature than 50°C resulted in a decrease of the yield of PAAm. These results of temperature dependence also support our concept that this polymerization is not a simple thermal polymerization, but a unique phenomenon concerned with the phase separation of aqueous PNIPAAm solutions at around LCST.

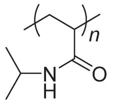
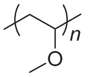
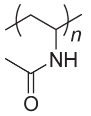
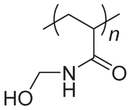
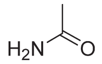
Moreover the mixing temperature and timing of AAm into aqueous PNIPAAm greatly influenced the polymerizability of AAm (Fig. 1, Table 3). Namely, AAm polymerized only when PNIPAAm and AAm were dissolved into water below LCST of PNIPAAm (32°C) and then the resulting clear solution was warmed to the polymerization temperature (40°C) (Table 3, method A, entry 1). On the other hand, the polymerization did not proceed when AAm was added into aqueous PNIPAAm solutions during and after the phase separation (Table 3, method B, entry 2). These results indicate



Additives: PNIPAAm, PVME, PNVA, PNHMAAm, acetamide

Sch. 1. Polymerization of AAm in the presence of several water soluble additives in water.

Table 1. Polymerization[a] of AAm in the presence of several water soluble additives

Entry	Additive	Yield of PAAm, %
1	—	0
2	 PNIPAAm	16.4
3	 PVME	13.8
4	 PNVA	<3
5	 PNHMAAm	0
6	 acetamide	0

[a]Polymerization conditions: Solvent, water; Total volume, 20 mL; Polymerization temperature, 30°C; Polymerization time, 40 h; Charged water soluble additives, 0.30 mol/L (based on the monomer units); Charged AAm, 0.30 mol/L.

Table 2. Temperature dependence of polymerization[a] of AAm in the presence of PNIPAAm[b]

Entry	Polymerization temperature, °C	Yield of AAm, %
1	20	0
2	30	16
	LCST (32°C)	
3	40	78
4	50	84
5	60	65

[a]Polymerization conditions: Solvent, water; Total volume, 20 mL; Charged AAm, 0.30 mol/L; Charged PNIPAAm, 0.30 mol/L (based on the monomer units); Polymerization temperature, 40°C; Polymerization time, 40 h.

[b]PNIPAAm was prepared by radical polymerization using AIBN as an initiator in THF. The number average molecular weight was determined to be 9400 by GPC.

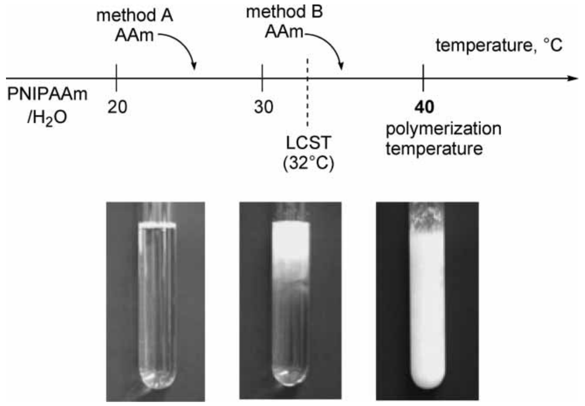


Fig. 1. Timing of the addition of AAm into an aqueous solution of PNIPAAm.

that the solution conditions of PNIPAAm in water at LCST play an important role to induce the polymerization of AAm.

3.3 Concentration Effect of Poly(N-isopropylacrylamide) on the Polymerization of Acrylamide

We have carried out the PNIPAAm ($\bar{M}n = 9400$) induced polymerization of AAm (0.30 mol/L) in water at 30°C varying the concentration of PNIPAAm from 0 up to 0.50 mol/L (based on the amount of the monomer units in PNIPAAm). Without PNIPAAm nor under lower concentration conditions polymerizations were not observed at all (Table 4, entries 1–3). The polymerization was induced in 0.30 mol/L or higher concentration solutions of PNIPAAm (Table 4, entries 4–6) and the yield of the resulting PAAm showed a maximum at 0.40 mol/L (Table 4, entry 5).

During the phase separation PNIPAAm chains in water aggregate to form a kind of matrix (19–21), and AAm monomers are probably concentrated in the PNIPAAm matrix. This matrix provides a rather hydrophobic reaction field and the interaction between AAm and the amide groups on PNIPAAm results in the generation of initiating radical species (5–8, 12, 13). This concentration effect and radical generation in the PNIPAAm matrix are supposed to induce the polymerization of AAm. At least equimolar amount of the monomer units of PNIPAAm to AAm monomers seem to be necessary to form the matrix that includes and concentrates enough amount of AAm to polymerize.

Table 3. Polymerization[a] of AAm in the presence of PNIPAAm[b]

Entry	Method[c]	Yield of PAAm, %
1	Method A	78
2	Method B	0

[a]Polymerization conditions: Solvent, water; Total volume, 20 mL; Charged AAm, 0.30 mol/L; Charged PNIPAAm, 0.30 mol/L (based on the monomer units); Polymerization temperature, 40°C; Polymerization time, 40 h.

[b]PNIPAAm was prepard by radical polymerization using AIBN as an initiator in THF. The number average molecular weight was determined to be 9400 by GPC.

[c]See Fig. 1.

Table 4. Effect of concentration of PNIPAAm on the polymerization of AAm in water[a]

Entry	Charged PNIPAAm[b], mol/L[c]	Yield of AAm, %
1	0	0
2	0.10	0
3	0.20	0
4	0.30	16
5	0.40	37
6	0.50	28

[a]Polymerization conditions: Solvent, water; Total volume, 20 mL; Charged AAm, 0.30 mol/L; Polymerization temperature, 30°C; Polymerization time, 40 h.

[b]PNIPAAm was prepard by radical polymerization using AIBN as an initiator in THF. The number average molecular weight was determined to be 9400 by GPC.

[c]Based on the monomer units of PNIPAAm.

3.4 Molecular Weight Dependence of the Polymerization of AAm in Aqueous Solutions of PNIPAAm

The polymerizability of AAm was remarkably influenced by the concentration and molecular weight of the PNIPAAm additives. Under the condition of lower PNIPAAm concentration (0.30 mol/L), the increase in the molecular weight of PNIPAAm considerably increased the molecular weight of the resulting PAAm, but decreased the yield of PAAm (Table 5, entries 1–3), Under the condition of higher PNIPAAm concentration (0.60 mol/L) the polymerizability was not as affected by the molecular weight of PNIPAAm, while the molecular weight of PAAm formed by using higher molecular weight PNIPAAm was higher than those of PAAm formed by using lower molecular weight PNIPAAm (Table 5, entries 4–6). The observed molecular weight dependence is probably due to the amount of AAm monomers included in the matrix that is produced by the aggregation of PNIPAAm chains in water at LCST. The matrix of higher molecular weight PNIPAAm includes and concentrates a larger amount of AAm monomers to afford high molecular weight PAAm. Moreover, the difference of the phase separation temperature of the PNIPAAm solutions seems to be related with the polymerizability of AAm. It has been reported (21) that the cloud point temperature for a given PNIPAAm gradually decreases with increasing the concentration from about 33°C down below 30°C, and also that the cloud point temperature is higher for PNIPAAm with higher molecular weight at the same concentration. It is reasonable that the yield of AAm is higher in the solution of lower molecular weight PNIPAAm because the inclusion of the AAm monomers in the matrix of PNIPAAm

Table 5. Molecular weight dependence of the polymerization[a] of AAm in aqueous solutions of PNIPAAm

	Charged PNIPAAm[b]		PAAm	
Entry	Molecular weight[c]	Concentration, mol/L[d]	Yield, %	$\bar{M}n^{e} \times 10^{-3}$
1	$\bar{M}n = 9400$ ($\bar{P}n = 83$), $\bar{M}w/\bar{M}n = 2.20$	0.30	78	1252
2	$\bar{M}n = 16100$ ($\bar{P}n = 142$), $\bar{M}w/\bar{M}n = 3.02$	0.30	38	2473
3	$\bar{M}n = 17400$ ($\bar{P}n = 154$), $\bar{M}w/\bar{M}n = 2.92$	0.30	22	3058
4	$\bar{M}n = 9400$ ($\bar{P}n = 83$), $\bar{M}w/\bar{M}n = 2.20$	0.60	72	1254
5	$\bar{M}n = 16100$ ($\bar{P}n = 142$), $\bar{M}w/\bar{M}n = 3.02$	0.60	59	1986
6	$\bar{M}n = 17400$ ($\bar{P}n = 154$), $\bar{M}w/\bar{M}n = 2.92$	0.60	60	2004

[a] Polymerization conditions: Solvent, water; Total volume, 20 mL; Charged AAm, 0.30 mol/L; Polymerization temperature, 40°C; Polymerization time, 40 h.

[b] PNIPAAm was prepard by radical polymerization using AIBN as an initiator in THF.

[c] Determined by GPC using THF as an eluent based on polystyrene standard.

[d] Based on the monomer units of PNIPAAm.

[e] Molecular weights ($\bar{M}n$) were estimated by using the formula, $[\eta] = 6.5 \times 10^{-3} \times \bar{M}n^{0.82}$ (Ref. 17). Intrinsic viscosities $[\eta]$ were determined by the standard technique using a Ostwald type viscometer.

Table 6. Comparison between several polymerization systems of AAm

		PAAm	
Entry	Polymerization system[a]	Yield, %	$\bar{M}n^{b} \times 10^{-3}$
1	PNIPAAm[c]/Water, 0.30 mol/L[d]	78	1252
2	AIBN/THF, 0.04 mol/L	95	20
3	VA-061[e]/Water, 0.02 mol/L	94	163

[a] Polymerization conditions: Solvent, water; Total volume, 20 mL; Charged AAm, 0.30 mol/L; Polymerization temperature, 40°C; Polymerization time, 40 h.

[b] Molecular weights ($\bar{M}n$) were estimated by using the formula, $[\eta] = 6.5 \times 10^{-3} \times \bar{M}n^{0.82}$ (Ref. 17). Intrinsic viscosities $[\eta]$ were determined by the standard technique using a Ostwald type viscometer.

[c] PNIPAAm was prepard by radical polymerization using AIBN as an initiator in THF. The number average molecular weight was determined to be 9400 by GPC.

[d] Based on the monomer units of PNIPAAm.

[e] 2,2′-Azobis[2-(2-imidazolin-2-yl)propane].

proceeds more smoothly at relatively low temperature. Under the condition of higher PNIPAAm concentration (0.60 mol/L), the phase separation temperature of the PNIPAAm solutions decreases affording PAAm in higher yield. Furthermore, the number of PNIPAAm molecules to form the matrix probably increases and it makes it possible to form larger size of matrix, which includes a larger amount of AAm monomers.

Table 6 shows the comparison between the polymerization of AAm in aqueous PNIPAAm solutions and the other conventional radical polymerizations of AAm in THF or water. It was remarkable that the molecular weight of PAAm formed by the PNIPAAm induced polymerization of AAm was much higher than that of the polymer obtained by the radical polymerization using AIBN in THF or VA-061 in water.

4 Conclusions

A unique polymerization system of AAm in aqueous solutions of PNIPAAm was found and the effects of polymerization temperature, concentration, and molecular weights of PNIPAAm on the polymerizability of AAm were demonstrated. This phenomenon was specifically observed in aqueous solutions of the polymers having lower critical solution temperature (LCST). The PNIPAAm molecular weight dependence of this polymerization was especially noted, namely, the increase in the molecular weight of PNIPAAm considerably increased the molecular weight of the resulting PAAm, but contrary decreased the yield of PAAm. The mechanism of this polymerization is not always clear at the presence, but the solution conditions of PNIPAAm in water at around its lower critical solution temperature (LCST, 32°C) is one of the most important factors to induce the polymerization. PNIPAAm chains in water aggregate to form a kind of matrix and AAm monomers are probably concentrated in the resulting matrix. The polymerization of AAm in the PNIPAAm matrix gives high molecular weight PAAm. In fact the molecular weight of PAAm formed by the PNIPAAm induced polymerization of AAm was much higher than that of the polymer obtained by usual polymerization using an radical initiator in water. From the synthetic point of view, the present polymerization method provides a new clean system to synthesis of high molecular weight PAAm since pure water is used as a solvent and PNIPAAm can be recycled. Moreover, there is a possibility to control the molecular weight of the resulting PAAm considering the observed molecular weight dependence in this polymerization system.

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