Hydrogen-Bond-Assisted Stereocontrol in the Radical Polymerization of *N*-Isopropylacrylamide with Secondary Alkyl Phosphate : Effect of Bulkiness of Ester Group

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Running Head: Hydrogen-bond-assisted stereocontrol

ABSTRACT: Radical polymerization of *N*-isopropylacrylamide (NIPAAm) in toluene at low temperatures was investigated in the presence of triisopropyl phosphate (T*i*PP). The addition of T*i*PP induced a syndiotactic-specificity that was enhanced by lowering polymerization temperature, whereas atactic polymers were obtained in the absence of T*i*PP regardless of temperature. Syndiotactic-rich poly(NIPAAm) with *racemo* diad = 65% was obtained at –60°C with a fourfold amount of T*i*PP, but almost atactic poly(NIPAAm)s were obtained by lowering temperature to –80°C. This result contrasted with the result in the presence of primary alkyl phosphates, such as tri-*n*-propyl phosphate, that stereospecificity varied from syndiotactic to isotactic by lowering polymerization temperature. NMR analysis at –80°C revealed that T*i*PP predominantly formed 1:1 complex with NIPAAm, although primary alkyl phosphates preferentially formed 1:2 complex with NIPAAm. Thus, it was concluded that a slight

increase in bulkiness of the added phosphates influenced the stoichiometry of the NIPAAm-phosphate complex at lower temperatures and consequently a drastic change in the effect on stereospecificity of NIPAAm polymerization was observed.

Keywords: hydrogen bond; *N*-isopropylacrylamide; phosphate; radical polymerization; stereospecific polymerization; syndiotactic

INTRODUCTION

In principle, *N*-monosubstituted acrylamides do not undergo vinyl polymerization via an anionic polymerization mechanism because of the acidic proton of amide group, although it was recently reported that bulky zincate could anionically polymerize *N*-isopropylacrylamide (NIPAAm).[1] Polymers of *N*-monosubstituted acrylamides are usually prepared by a radical polymerization so that the stereoregularity of polymers derived from *N*-monosubstituted acrylamides have attracted less attention in comparison with that derived from other α,β-unsaturated carbonyl monomers such as (meth)acrylates.[2-10] However, some methods to control stereostructure of poly(*N*-monosubstituted acrylamide)s have been reported in recent years. For instance, both isotactic and syndiotactic poly(NIPAAm)s were prepared by an anionic polymerization of NIPAAm, the acidic proton of which was protected.[11,12] Moreover, the use of Lewis acid such as yttrium trifluoromethanesulfonate afforded isotactic poly(*N*-monosubstituted acrylamide)s even by a radical polymerization mechanism.[13,14]

On the other hand, *N,N*-disubstituted acrylamides undergo an anionic polymerization, since the acidic proton of amide group is substituted. Several stereospecific anionic polymerizations of *N,N*-disubstituted acrylamides have been reported.[11,12,15-18] Furthermore, there are a few reports on stereocontrol even for a radical polymerization of *N,N*-disubstituted acrylamide, based on the chirality[19] or the bulkiness[20] of the substituents. It was reported that *N*-monosubstituted acrylamides

favor *s-cis* C=C-C=O and *s-trans* O=C-N-H conformations and *N,N*-disubstituted acrylamides favor *s-cis* C=C-C=O conformation.[21]   Thus, it is assumed that the steric interaction by the second substituent at the amide nitrogen atom is a very important factor for the stereocontrol in polymerization of acrylamide derivatives.
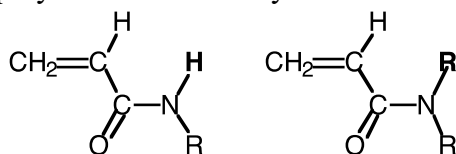

Recently, we succeeded in controlling the stereostructure of radically prepared poly(NIPAAm)s utilizing a hydrogen-bond-assisted complex formation between NIPAAm monomer and Lewis bases as follows.   The addition of a twofold amount of hexamethylphosphoramide (HMPA) in toluene at –60°C afforded a syndiotactic-rich poly(NIPAAm) with *racemo* (*r*) diad of 70%.[22,23]   A stereocontrol from syndiotactic-rich to isotactic-rich was also achieved by changing the polymerization temperature in the presence of a fourfold amount of primary alkyl phosphate, such as trimethyl phosphate, triethyl phosphate (TEP), tri-*n*-propyl phosphate (TPP), and tri-*n*-butyl phosphates (TBP).[24]   For instance, syndiotactic-rich poly(NIPAAm) with *r* diad of 65% was obtained with TEP at –40°C and isotactic-rich poly(NIPAAm) with *meso* (*m*) diad of 57% with TBP at –80°C.   ^{1}H NMR signal due to the amide proton of NIPAAm was shifted downfield by the addition of such phosphoric acid derivatives. Thus, it is suggested that the added Lewis bases behaved like the second substituent at the amide nitrogen by coordinating through a hydrogen-bonding interaction.
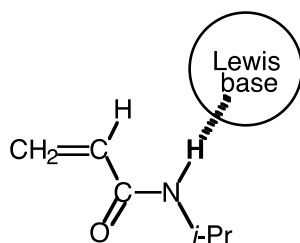
Furthermore, the NMR analysis demonstrated that NIPAAm and HMPA formed 1:1 complex through a hydrogen-bonding interaction at –80 to 0°C,[22,23] whereas the stoichiometry of NIPAAm-TBP complexes changed from 1:1 to 1:2 with a decrease

in temperature.[24]   Thus, it is assumed that the stereospecificity of NIPAAm polymerization depends not only on hydrogen-bond-assisted complex formation but also on the stoichiometry of the complex; that is, 1:1 complexed monomer favors a syndiotactic-specific propagation and 1:2 complexed monomer favors an isotactic-specific propagation.

1:1 Complex   **1:2 Complex**

⇩   ⇩

Syndiotactic   **Isotactic**
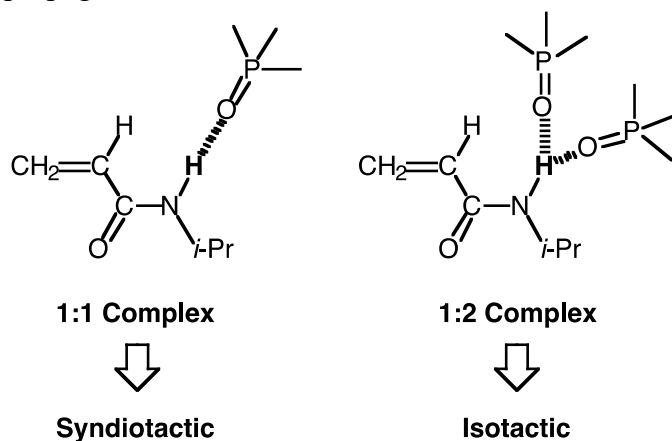
In this article, we conducted radical polymerizations of NIPAAm in the presence of triisopropyl phosphate (TiPP) as a branched and bulkier ester.   A significant effects of bulkiness of the added phosphate on the stoichiometry of the hydrogen-bond-assisted complex and hence on the stereospecificity of NIPAAm polymerization were observed.

EXPERIMENTAL

NIPAAm was recrystallized from hexane-benzene mixture.   Toluene was purified through washing with sulfuric acid, water, and 5% aqueous NaOH; this was followed by fractional distillation.   Tri-n-butylborane (n-Bu$_3$B) as a tetrahydrofuran (THF) solution (1.0M) and TiPP were commercially obtained and used without further purification for polymerization reaction.

Typical polymerization procedure is as follows; NIPAAm (0.314 g, 2.8 mmol) was dissolved in toluene to prepare the 5 mL solution of 0.56 mol/L.   Four milliliter of the solution was transferred to the glass ampoule and cooled at 0°C.   The

polymerization was initiated by adding n-Bu$_3$B solution (0.22 ml) into the monomer solution.   After 24h, the reaction was terminated with a small amount of THF solution of 2,6-di-t-butyl-4-methylphenol at polymerization temperature.   The polymerization mixture was poured into a large amount of hexane or hexane-ethyl acetate mixture (9:1 vol:vol), and the precipitated polymer was collected by filtration or centrifugation, and dried *in vacuo*.   The polymer yield was determined from the weight ratio of the obtained polymer and the feed monomer.

The ^{1}H and ^{13}C NMR spectra of NIPAAm monomer and/or TiPP were measured in toluene-d_8 at –80°C to 60°C on an EX-400 spectrometer (JEOL Ltd.) operated at 400MHz for ^{1}H and at 100MHz for ^{13}C.   The tacticities of the poly(NIPAAm)s were determined from ^{1}H NMR signals due to methylene group in chain measured in deuterated dimethyl sulfoxide (DMSO-d_6) at 150°C.   The molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography (SEC) (HLC 8220 instrument (Tosoh Co.)) equipped with TSK gels (SuperHM-M and SuperHM-H (Tosoh Co.)) using dimethylformamide (LiBr 10 mmol/L) as an eluent at 40°C ([polymer] = 1.0 mg/mL, flow rate = 0.35 mL/min). The SEC chromatogram was calibrated with standard polystyrene samples.

RESULTS AND DISCUSSION

Radical Polymerization of NIPAAm in the Presence of TiPP

Table 1 summarizes the results of radical polymerization of NIPAAm in toluene at low temperatures for 24h in the absence or presence of TiPP.   In the absence of TiPP, polymer yield drastically decreased as the polymerization temperature was lowered, probably because monomer and/or polymer were precipitated during the polymerization reaction.   However, polymer yields increased even at low temperatures in the presence of TiPP similar to the cases of other phosphoric acid derivatives[23,24] since the addition of TiPP improved the solubility of NIPAAm and/or poly(NIPAAm) in toluene through

a coordination. The addition of T*i*PP showed a tendency to decrease number-average molecular weights (M_n) and molecular weight distributions of the obtained poly(NIPAAm)s regardless the polymerization temperature. Thus, it is suggested that T*i*PP also exhibits a certain significant effect in NIPAAm polymerization.

The syndiotacticity of the poly(NIPAAm)s obtained in the presence of T*i*PP was higher than that of poly(NIPAAm)s obtained in the absence of T*i*PP. The magnitude of the increased syndiotacticity was enhanced with an increase in the added amount of T*i*PP, although those with equimolar and twofold amounts of T*i*PP were relatively small. Syndiotactic-rich poly(NIPAAm) with r = 65% was obtained at – 60°C in the presence of a fourfold amount of T*i*PP.

<Table 1>

Figure 1 displays the relationship between polymerization temperature and r diad content of poly(NIPAAm) prepared in the absence or presence of a fourfold amount of T*i*PP. The data obtained in the presence of a fourfold amount of straight alkyl phosphate, TPP, were also plotted. Little difference was observed in syndiotacticity of poly(NIPAAm)s obtained at –40 to 0°C regardless of the kind of the added phosphate. However, syndiotactic-rich poly(NIPAAm) was obtained even below –40°C in the presence of T*i*PP, although isotactic-rich poly(NIPAAm) was obtained at –80°C in the presence of TPP.[24] This result suggests that a slight difference in bulkiness of the added phosphates drastically affects the stereospecificity of NIPAAm polymerization.

<Figure 1>

Stoichiometry of NIPAAm-T*i*PP Complex

Regardless of polymerization temperature, HMPA formed 1:1 complex with NIPAAm

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and syndiotactic-rich poly(NIPAAm)s were obtained.[23]   On the other hand, NIPAAm and primary alkyl phosphates predominantly formed 1:1 complex at 0°C, where syndiotactic-rich poly(NIPAAm)s were obtained, but formed 1:2 complex at –80°C, where isotactic-rich poly(NIPAAm)s were obtained.[24]   Therefore, it is assumed that a difference in the stoichiometry between NIPAAm-TiPP complex and NIPAAm-TPP complex attributes such a drastic change in the temperature dependence of stereospecificity of NIPAAm polymerization (cf. Figure 1).   Thus, we conducted ^{13}C NMR analysis under the following conditions, $[NIPAAm]_0 + [TiPP]_0 = 0.25$ mol/L, in toluene-d_8 at desired temperatures, to investigate the stoichiometry of the NIPAAm-TiPP complex.

Figure 2 shows changes in the chemical shift of methylene carbon of NIPAAm at 0°C.   The signal was linearly shifted to a lower magnetic field as the fraction of $[NIPAAm]_0$ decreased.   The stoichiometry of the complex was evaluated by Job's method (Figure 3) with the following eq. (1);[25]

$$[NIPAAm - TiPP] = \frac{\delta(CH_2=) - \delta(CH_2=)_f}{\delta(CH_2=)_c - \delta(CH_2=)_f} \times [NIPAAm]_0 \quad (1)$$

where $\delta(CH_2=)$ and $\delta(CH_2=)_f$ are the chemical shifts of methylene carbon of the sample mixture and NIPAAm alone, respectively.   As previously reported,[22-24] the chemical shift of NIPAAm alone also varied with the concentration (Figure 2), because NIPAAm itself also associates each other through a hydrogen-bonding interaction.   Thus, the chemical shifts of NIPAAm alone at the corresponding concentration were applied as $\delta(CH_2=)_f$.   The chemical shift for the saturated mixture ($\delta(CH_2=)_c$) was calculated from the intercept of the linear dependence in Figure 2, since a saturation should be independent of NIPAAm concentration.   The maximum was observed at 0.5 of the $[NIPAAm]_0$ fraction (Figure 3).   Thus, it is thought that TiPP forms 1:1 complex with NIPAAm at 0°C, corresponding to the results with other phosphoric acid derivatives.[22,24]

<Figure 2>

<Figure 3>

At –80°C, the change in the chemical shift of carbonyl carbon was large enough to be applied to Job's plots, whereas that of the methylene carbon was too small. Thus, we applied the chemical shift of the carbonyl carbon to Job's plots to evaluate the stoichiometry at –80°C.   Figure 4 demonstrates changes in the chemical shift of the carbonyl carbon of NIPAAm in the presence of TiPP ([NIPAAm]$_0$ + [TiPP]$_0$ = 0.25 mol/L) and of NIPAAm alone at the corresponding concentration.   The chemical shift was significantly shifted upfield with a decrease in [NIPAAm]$_0$ in the presence of TiPP in comparison with the shift in the absence of TiPP.   The plots roughly obeyed not a linear equation but a quadratic equation.   Thus, the chemical shift for the saturated mixture (δ(C=O)$_c$) was calculated from the intercept of a quadratic dependence in Figure 4.   Unlike at 0°C, the calculated data were asymmetrically plotted and a broad maximum was observed between 0.4 and 0.5 of the [NIPAAm]$_0$ fraction (Figure 5). This means that NIPAAm and TiPP afford both 1:1 and 1:2 complexes at –80°C, but the 1:1 complex is preferentially formed.   NIPAAm and primary alkyl phosphates also afford both 1:1 and 1:2 complexes at –80°C, but the 1:2 complex is predominantly formed.[24]   Thus, it is indicated that a slight difference in bulkiness of the added phosphates influences the stoichiometry of the hydrogen-bond-assisted complex and consequently a drastic change in the stereospecificity was observed at lower temperatures (Scheme 1).

<Scheme 1>

Equilibrium Constant (K) of the Complex between NIPAAm and TiPP

It was found that T*i*PP also formed 1:1 complex with NIPAAm at 0°C.   Therefore, we determined the equilibrium constant of the NIPAAm-T*i*PP complex above 0°C.   The equilibrium constant (K) of the NIPAAm-T*i*PP complex was determined by changes in the ^{1}H NMR chemical shift of amide proton of NIPAAm.   Figure 6 demonstrates the relationship between the change in the chemical shift and the ratio of $[TiPP]_0/[NIPAAm]_0$ with the constant concentration of $[NIPAAm]_0$ (5.0×10^{-2} mol/L) in toluene-d_8 at several temperatures. The equilibrium constants (K) (Table 2) were determined by the analysis of the data in Figure 6 by a nonlinear least-squares fitting to the following eq. (2):[26]

$$\Delta\delta = \frac{\Delta\delta'}{2}\left(b - \sqrt{b^2 - 4X} \right) \quad (2)$$

$$b = 1 + X + \frac{1}{(K\,[NIPAAm]_0)}$$

$$X = [TiPP]_0 / [NIPAAm]_0$$

where $\Delta\delta$ and $\Delta\delta'$ are the changes in the chemical shift of amide proton of NIPAAm for the given solution and a saturated solution, respectively.   For instance, the K value at 0°C was found to be 12.6 L/mol.   This value was quite smaller than that for HMPA (44.0 L/mol)[22] but comparable with those for primary alkyl phosphates (5.96 ~ 15.3 L/mol).[24]   Interestingly, the K value for TPP was calculated to be 12.8 L/mol.   Thus, it is suggested that the equilibrium at 0°C depends on the basicity of the added Lewis base rather than the bulkiness of the added Lewis base, although the stoichiometry at lower temperatures strongly depends on the bulkiness of the added Lewis base.

<Figure 6>

<Table 2>

The enthalpy (ΔH) and the entropy (ΔS) for the 1:1 complex formation were determined to be $-(19.8 \pm 0.73)$ kJ/mol and -51 ± 2 J/mol•K, respectively, from the

van't Hoff's plots for the obtained K values according to the following eq. (3):

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (3)$$

where R is a gas constant (8.315 J/mol•K) and T is the absolute temperature (K). These values were also similar to those for TPP (ΔH: –20.0 ± 0.75 kJ/mol and ΔS: –52 ± 2 J/mol•K). This result also suggests that 1:1 complex formation depends on the basicity of the added Lewis base.

On the assumption that NIPAAm and TiPP formed 1:1 complex even below 0°C and ΔH is constant from –60°C to 60°C, we calculated K values below 0°C according to eq. (3). The calculated values are summarized in Table 2 together with the obtained values for 0°C to 60°C. Regardless of the amount of the added TiPP, the fraction of complex should increase as the polymerization temperature was lowered. However, the obtained syndiotacticity hardly varied in the temperature range from –60 to 0°C in the presence of equimolar or twofold amounts of TiPP. In this polymerization system, a propagating reaction should proceed via four possible routes (**A-D**) as shown Scheme 2. Route **A** should be atactic, because atactic polymers are obtained in the absence of Lewis bases. Although the stereospecificity of routes **B** and **C** are not clear, it is suggested that 1:1 complex formation of both the radical and the monomer with TiPP (**D**) is necessary for a syndiotactic-specific propagation, based on the fact that a large excess amount of TiPP was required for a significant induction of the syndiotactic-specificity.

<Scheme 2>

The Role of TiPP Estimated from the Viewpoint of Thermodynamics

The syndiotacticity of the poly(NIPAAm)s obtained in the presence of a fourfold amount of TiPP linearly increased as the polymerization temperature was lowered until

–60°C. To determine the apparent difference in activation enthalpy ($\Delta H^{\ddagger}$) and the apparent difference in activation entropy ($\Delta S^{\ddagger}$) between isotactic and syndiotactic propagations in the presence of a fourfold amount of TiPP, we conducted Fordham's plots according to the following equation (4): [27]

$$\ln\left(\frac{P_i}{P_s}\right) = \frac{\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}}{R} - \frac{\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}}{RT} \quad (4)$$

where P_i and P_s denote the mole fractions of isotactic and syndiotactic diads, respectively. The apparent $\Delta H_i^{\ddagger}$ - $\Delta H_s^{\ddagger}$ and the apparent $\Delta S_i^{\ddagger}$ - $\Delta S_s^{\ddagger}$ were determined to be 1.04 ± 0.05 kJ/mol and –0.3 ± 0.2 J/mol•K. The apparent $\Delta H_i^{\ddagger}$ - $\Delta H_s^{\ddagger}$ was large as compared with the $\Delta H_i^{\ddagger}$ - $\Delta H_s^{\ddagger}$ in the absence of TiPP (0.03 ± 0.01 kJ/mol), although the value was smaller than those with HMPA (1 equiv. 1.85 ± 0.14 kJ/mol; 2 equiv. 2.31 ± 0.09 kJ/mol).[23] This result is consistent with the results observed in syndiotactic-specific radical polymerization of N,N-diphenylacrylamide.[20] Thus, it is suggested that the syndiotactic-specificity was educed by the coordinating TiPP behaving like the second substituent at the nitrogen amide atom, as expected. The absolute value of the apparent $\Delta S_i^{\ddagger}$ - $\Delta S_s^{\ddagger}$ was smaller than the $\Delta S_i^{\ddagger}$ - $\Delta S_s^{\ddagger}$ in the absence of TiPP (–1.5 ± 0.0 J/mol•K), although both values were negative. In previous papers, we proposed a mechanism for the syndiotactic-specific polymerization, in which a propagating reaction proceeds between a complexed monomer and a radical conformationally fixed due to the steric repulsion between the amide group at the chain-end monomeric unit and the added Lewis base coordinating to the penultimate monomeric unit (Scheme 3).[23,24] Taking into consideration that the addition of HMPA afforded positive apparent $\Delta S_i^{\ddagger}$ - $\Delta S_s^{\ddagger}$ values,[23] it is suggested that the coordination of TiPP also retarded the rotation near the propagating chain-end and then the syndiotactic-specificity was induced, although the effect was weaker than that with HMPA.

<Scheme 3>

CONCLUSIONS

Radical polymerizations of NIPAAm were examined in the presence of T*i*PP, a branched ester of phosphoric acid.   The addition of secondary alkyl ester of phosphoric acid afforded syndiotactic-rich poly(NIPAAm) at –80°C to 0°C, whereas isotactic-rich poly(NIPAAm) was obtained in the presence of primary alkyl ester of phosphoric acid at –80°C.   NMR analysis demonstrated that secondary alkyl phosphate favored 1:1 complex formation even at –80°C, although primary alkyl phosphates favored 1:2 complex formation at –80°C.   Thus, it was revealed that a slight increase in bulkiness of the added phosphate influenced the stoichiometry of NIPAAm-phosphate complexes and consequently exhibited a drastic change in the effect on the stereospecificity of NIPAAm polymerization.   Now, further work is under way to investigate the effect of further bulkier phosphates on the stereospecificity of NIPAAm polymerization.

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Captions for Figures and Schemes

Figure 1. Relationship between the polymerization temperature and r diad content of poly(NIPAAm) prepared in toluene at low temperatures in the absence or presence of a fourfold amount of TiPP or TPP.

Figure 2. Changes in the methylene carbon chemical shifts of NIPAAm in the presence of TiPP (■) ([NIPAAm]$_0$ + [TiPP]$_0$ = 0.25 mol/L) and of NIPAAm alone at the corresponding concentration (●), as measured in toluene-d_8 at 0°C.

Figure 3. Job's plots for the association of NIPAAm with TiPP at 0°C evaluated from the changes in the chemical shift of methylene carbon of NIPAAm.

Figure 4. Changes in the carbonyl carbon chemical shifts of NIPAAm in the presence of TiPP (■) ([NIPAAm]$_0$ + [TiPP]$_0$ = 0.25 mol/L) and of NIPAAm alone at the corresponding concentration (●), as measured in toluene-d_8 at –80°C.

Figure 5. Job's plots for the association of NIPAAm with TiPP at –80°C evaluated from the changes in the chemical shift of carbonyl carbon of NIPAAm.

Figure 6. Changes in the chemical shift of the amide proton of NIPAAm in the presence of TiPP, as measured in toluene-d_8 at various temperatures.

Scheme 1. Effect of bulkiness of the added phosphate on the stoichiometry of the NIPAAm-phosphate complex at lower temperatures.

Scheme 2. Four possible propagation routes in NIPAAm polymerization in the presence of TiPP.

Scheme 3. Proposed mechanism for the syndiotactic-specific propagation between a complexed monomer and a radical conformationally fixed by the coordination with T*i*PP.

Table 1. Radical Polymerization of NIPAAm in toluene at low temperatures for 24h in the absence or presence of TiPP[a]

Run	[TiPP]/[NIPAAm]	Temperature °C	Yield %	Diad tacticity/%[b] m	r	M_n[c] x 10^4	M_w/M_n[c]
1 [d]	0	0	>99	46	54	2.87	3.5
2 [d]	0	−20	>99	46	54	2.38	3.1
3 [d]	0	−40	75	44	56	2.39	2.7
4 [d]	0	−60	41	44	56	2.47	3.0
5 [d]	0	−80	18	44	56	1.72	3.2
6	1	0	>99	42	58	1.15	2.1
7	1	−20	>99	41	59	1.08	5.6
8	1	−40	>99	41	59	1.17	2.0
9	1	−60	88	43	57	1.25	1.9
10 [d]	1	−80	41	43	57	1.43	4.8
11	2	0	88	41	59	1.22	2.4
12	2	−20	97	39	61	1.15	2.7
13	2	−40	96	39	61	1.05	1.8
14	2	−60	95	39	61	1.35	1.8
15 [d]	2	−80	>99	44	56	1.14	1.9
16	4	0	>99	38	62	0.98	1.9
17	4	−20	>99	37	63	1.15	1.7
18	4	−40	>99	36	64	1.36	1.7
19	4	−60	>99	35	65	1.74	2.2
20	4	−80	93	43	57	0.86	2.8

a. [NIPAAm]$_0$ = 0.5 mol/L, [n-Bu$_3$B] = 0.05 mol/L.

b. Determined by ^{1}H NMR signals due to methylene group.

c. Determined by SEC (polystyrene standards).

d. The monomer, polymer or both were precipitated during the polymerization reaction.

Table 2. (Calculated) equilibrium constants (K) for the interaction between NIPAAm and TiPP and (calculated) degree of association (α) in the polymerization system[a]

Temperature	K		α[b]		
°C	L/mol	(TiPP)	1 equiv.	2 equiv.	4 equiv.
60	2.59		0.43	0.64	0.81
40	4.36		0.51	0.73	0.87
25	6.41		0.58	0.79	0.91
0	12.6		0.67	0.88	0.95
–20	(25.7)[c]		0.76	0.93	0.97
–40	(57.8)[c]		0.83	0.97	0.99
–60	(151)[c]		0.89	0.99	1.00

a. NMR conditions; $[\text{NIPAAm}]_0 = 5.0 \times 10^{-2}$ mol/l, toluene-d_8.

b. Calculated with $[\text{NIPAAm}]_0 = 0.5$ mol/l.

c. Calculated from van't Hoff relationship.

Figure 1 / T. Hirano et al.
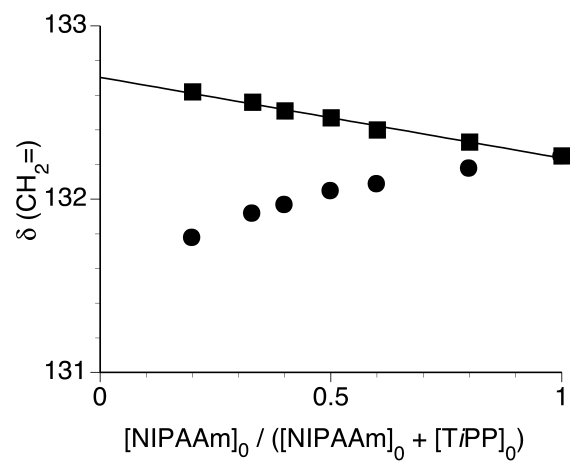
Figure 2 / T. Hirano et al.

δ (CH$_2$=)

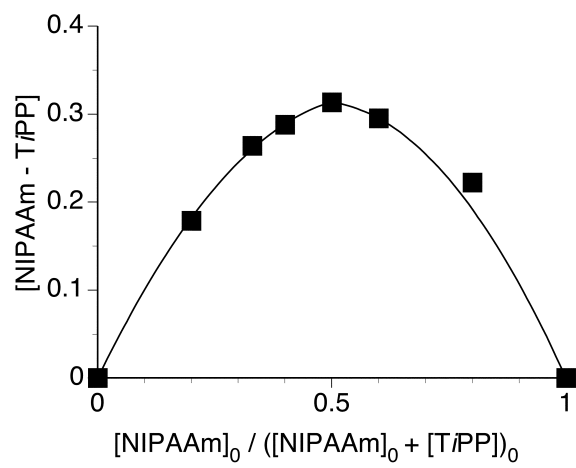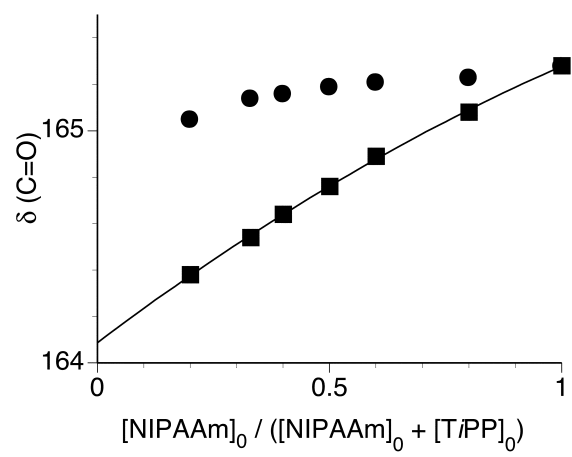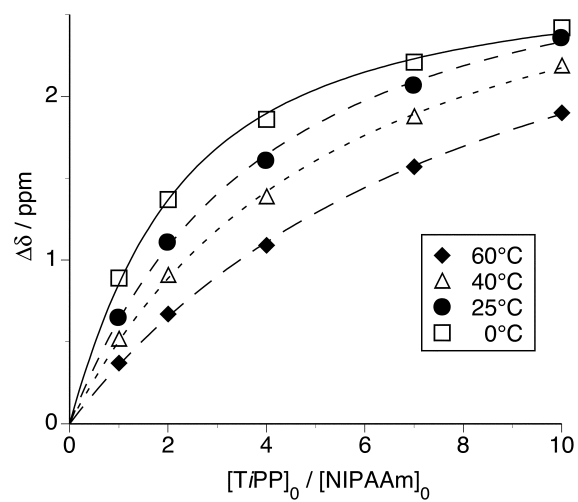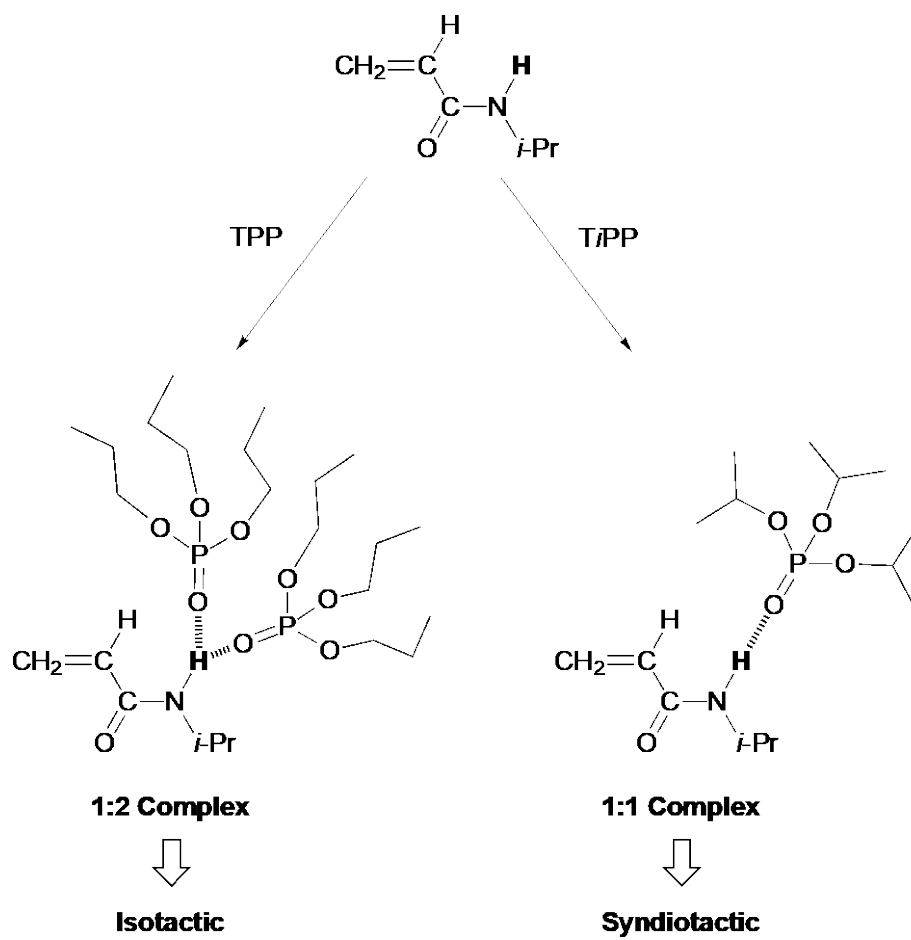[NIPAAm]$_0$ / ([NIPAAm]$_0$ + [TiPP]$_0$)

Figure 3 / T. Hirano et al.

Plot with y-axis labeled "[NIPAAm - TiPP]" ranging from 0 to 0.4, and x-axis labeled "[NIPAAm]$_0$ / ([NIPAAm]$_0$ + [TiPP])$_0$" ranging from 0 to 1.

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Plot with y-axis labeled δ (C=O) ranging from 164 to 165, and x-axis labeled $[NIPAAm]_0 / ([NIPAAm]_0 + [TiPP]_0)$ ranging from 0 to 1.

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[NIPAAm]$_0$ / ([NIPAAm]$_0$ + [T*i*PP])$_0$

Figure 6 / T. Hirano et al.

Scheme 1 / T. Hirano et al.

1:2 Complex

⬇

Isotactic

1:1 Complex

⬇

Syndiotactic

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