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Hydrogen-bond-assisted stereocontrol in the radical polymerization of *N*-isopropylacrylamide with bidentate Lewis base

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Abstract

Radical polymerization of *N*-isopropylacrylamide (NIPAAm) in toluene was investigated in the presence of bidentate Lewis base such as diphosphonates. Isotacticity of the obtained poly(NIPAAm)s slightly increased at −80 °C, whereas syndiotactic-rich poly(NIPAAm)s were obtained at −40–0 °C. This result corresponded to the results observed in the presence of primary alkyl phosphates. NMR analysis revealed that NIPAAm monomer and tetraisopropyl methylenebisphosphonate formed mono-binding hydrogen-bond-assisted complex at 0 °C, but a chelate complex at −80 °C. Thus, it was concluded that the stereospecificity in NIPAAm polymerization strongly depended on the complexation mode of the added bidentate Lewis base.

Keywords: Hydrogen bond; Stereospecific radical polymerization; Chelate complex

1. Introduction

In principle, *N*-isopropylacrylamide (NIPAAm) does not undergo vinyl polymerization via an anionic polymerization mechanism because of the acidic proton of amide group [1]. Thus, poly(NIPAAm) is usually prepared by a radical polymerization so that the stereoregularity of poly(NIPAAm) has attracted less attention in comparison with those derived from other α,β-unsaturated carbonyl monomers such as (meth)acrylates [2–10]. However, some methods to control stereostructure of poly(NIPAAm) have been reported in recent years. An anionic polymerization of trimethylsilyl-protected NIPAAm derivative with *t*-C_4H_9Li/*n*-$(C_4H_9)_3Al$ in toluene at −40 °C followed by deprotection produced an isotactic poly(NIPAAm) with *meso* (*m*) diad content of 97% [11]. An anionic polymerization of *N*-isopropyl-*N*-methoxymethylacrylamide with alkyllithium/diethylzinc followed by deprotection afforded a syndiotactic poly(NIPAAm) with *racemo* (*r*) diad of 75% [12]. Moreover, an addition of Lewis acid such as yttrium trifluoromethanesulfonate directly gave isotactic poly(NIPAAm)s over *m* diad of 90% even by a radical polymerization mechanism [13,14]. In all the cases, however, metal complexes played important roles for the stereocontrol, although isolation of the resulting polymer is difficult due to strong interaction between metal compounds and polymer materials. Thus, development of metal-free stereospecific polymerization system has been strongly desired.

Recently, we found that stereostructure of radically prepared poly(NIPAAm)s could be controlled even under metal-free conditions by utilizing a hydrogen-bond-assisted complex formation between NIPAAm monomer and Lewis bases [15–19]. The addition of a fivefold amount of hexamethylphosphoramide (HMPA) in toluene at −60 °C afforded a syndiotactic-rich poly(NIPAAm) with *r* diad of 72% [19]. Although bulkier ester derivatives such as triisopropyl phosphate (T*i*PP), as well as HMPA, afforded syndiotactic-rich poly(NIPAAm)s regardless of temperature [18], primary alkyl phosphates exhibited more complicated effect on the stereospecificity; an isotactic-rich poly(NIPAAm) with *m* diad of 57% was obtained in the presence of a fourfold amount of tri-*n*-butyl phosphate (TBP) at −80 °C, whereas syndiotactic-rich poly(NIPAAm)s ($r \geq 63\%$) were obtained at −40–0 °C under the same conditions [17].

NMR analyses demonstrated that NIPAAm and HMPA formed 1:1 complex through a hydrogen-bonding interaction at −80–0 °C [15,16], whereas the stoichiometry of NIPAAm-TBP complexes changed from 1:1 to 1:2 with a decrease in

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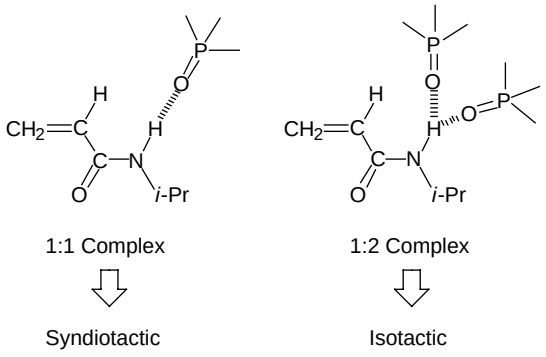
temperature [17]. Thus, it was assumed that the stereospecificity of NIPAAm polymerization depended not only on hydrogen-bond-assisted complex formation but also on the stoichiometry of the complex; 1:1 complexed monomer favored a syndiotactic-specific propagation and 1:2 complexed monomer favored an isotactic-specific propagation.

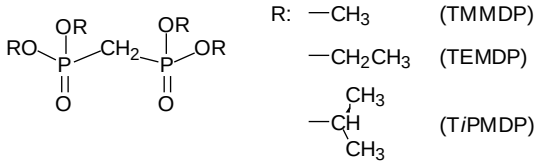


For the formation of 1:2 complexed monomer, the second Lewis base have to approach the 1:1 complexed monomer bulkier than free NIPAAm monomer. Thus, it is assumed that the 1:2 complex formation is difficult as compared with the 1:1 complex formation and consequently the isotactic-specificity was induced only when an excess amount of less bulky Lewis base was added at low temperature such as −80 °C. In this article, we conducted radical polymerizations of NIPAAm in the presence of bidentate Lewis base, such as tetraalkyl methylenebisphosphonates, because easier formation of the 1:2 complex is expected due to a chelate effect. Then, we observed an increase in the isotacticity of poly(NIPAAm)s obtained at −80 °C even in the presence of equimolar amount of bulky bidentate Lewis base.

2. Experimental section

2.1. Materials

N-Isopropylacrylamide (NIPAAm) (Tokyo Kasei Kogyo Co.) 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_3B) as a tetrahydrofuran (THF) solution (1.0 M) (Aldorich Chemical Co.), tetamethyl methylenebisphosphonate (TMMDP), tetraethyl methylenebisphosphonate (TEMDP) (Lancaster Synthesis Ltd), and tetraisopropyl methylenebisphosphonate (T*i*PMDP) (Tokyo Kasei Kogyo Co.) were commercially obtained and used without further purification for polymerization reaction.



2.2. Polymerization

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_3B solution (0.22 ml) into the monomer solution. After 24 h, 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

Table 1
Radical polymerization of NIPAAm in toluene at different temperatures for 24 h in the absence or presence of TMMDP

Run	$[TMMDP]_0$ (mol/l)	Temp. (°C)	Yield (%)	Diad tacticity (%)[a]		M_n[b] × 10^4	M_w/M_n[b]
				m	*r*		
1[c]	0.0	0	>99	46	54	2.87	3.5
2[c]	0.0	−20	>99	46	54	2.38	3.1
3[c]	0.0	−40	75	44	56	2.39	2.7
4[c]	0.0	−60	41	44	56	2.47	3.0
5[c]	0.0	−80	18	44	56	1.72	3.2
6	0.5	0	>99	42	58	1.93	1.6
7	0.5	−20	>99	42	58	1.53	1.4
8	0.5	−40	>99	42	58	1.86	1.6
9	0.5	−60	>99	46	54	1.76	1.7
10	0.5	−80	>99	48	52	2.54	1.4
11	1.0	0	>99	39	61	2.11	1.3
12	1.0	−20	>99	39	61	1.53	1.4
13	1.0	−40	>99	39	61	3.00	1.5
14	1.0	−60	97	46	54	2.58	1.6
15	1.0	−80	90	48	52	2.22	2.0

$[NIPAAm]_0 = 0.5$ mol/l, $[n\text{-}Bu_3B]_0 = 0.05$ mol/l.
[a] Determined by ^1H NMR signals due to methylene group.
[b] Determined by SEC (polystyrene standards).
[c] The monomer, polymer, or both were precipitated during the polymerization reaction.

Table 2
Radical polymerization of NIPAAm in toluene at different temperatures for 24 h in the presence of TEMDP

Run	$[TEMDP]_0$ (mol/l)	Temp. (°C)	Yield (%)	Diad tacticity (%)[a]		M_n[b]$\times 10^4$	M_w/M_n[b]
				m	*r*		
1	0.5	0	81	39	61	1.61	1.7
2	0.5	−20	>99	39	61	1.24	1.6
3	0.5	−40	>99	38	62	1.18	1.8
4	0.5	−60	>99	40	60	1.31	1.7
5[c]	0.5	−80	92	42	58	1.43	1.9
6	1.0	0	87	39	61	1.80	1.6
7	1.0	−20	94	38	62	1.56	1.6
8	1.0	−40	>99	37	63	1.30	1.8
9	1.0	−60	>99	39	61	2.56	2.1
10[c]	1.0	−80	>99	48	52	1.10	1.7

$[NIPAAm]_0 = 0.5$ mol/l, $[n\text{-}Bu_3B]_0 = 0.05$ mol/l.
[a] Determined by ^1H NMR signals due to methylene group.
[b] Determined by SEC (polystyrene standards).
[c] The monomer, polymer, or both were precipitated during the polymerization reaction.

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.

2.3. Measurements

The ^{13}C NMR spectra of NIPAAm monomer, T*i*PMDP, or both were measured in toluene-d_8 at the desired temperatures on an EX-400 spectrometer (JEOL Ltd) operated at 100 MHz. The tacticities of the poly(NIPAAm)s were determined from ^1H 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.

3. Results and discussion

3.1. NIPAAm polymerization in the presence of bidentate Lewis base

Table 1 summarizes the results of radical polymerization of NIPAAm in the absence or presence of TMMDP at the temperature range from −80 to 0 °C. The addition of TMMDP increased polymer yield as well as monodentate Lewis bases such as trimethyl phosphate (TMP), probably because of the improvement in the solubility of NIPAAm and/or poly (NIPAAm) in toluene. The number average molecular weight (M_n) increased as the amount of the added TMMDP increased,

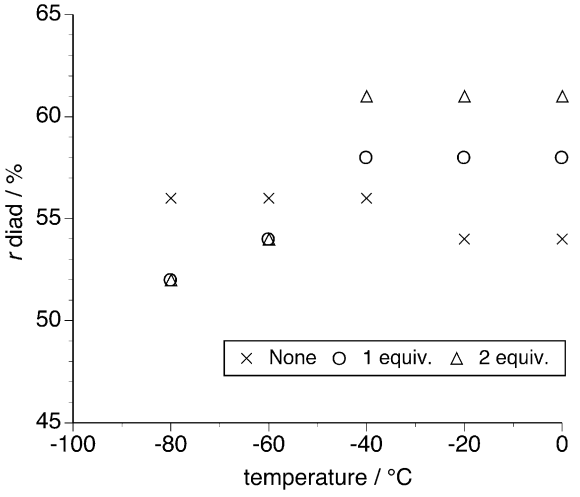


Fig. 1. Relationship between the polymerization temperature and *r* diad content of poly(NIPAAm) prepared in toluene at low temperatures in the presence of TMMDP.

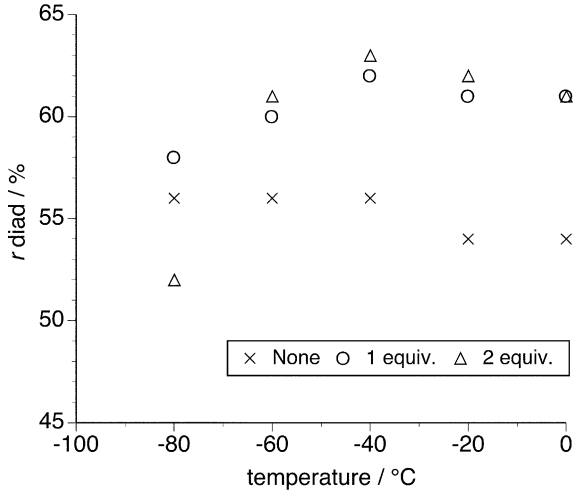


Fig. 2. Relationship between the polymerization temperature and *r* diad content of poly(NIPAAm) prepared in toluene at low temperatures in the presence of TEMDP.

Table 3
Radical polymerization of NIPAAm in toluene at different temperatures for 24 h in the presence of T*i*PMDP

Run	$[Ti\text{PMDP}]_0$ (mol/l)	Temp. (°C)	Yield (%)	Diad tacticity (%)[a]		M_n[b] $\times 10^4$	M_w/M_n[b]
				m	*r*		
1	0.5	0	98	40	60	1.25	2.0
2	0.5	−20	>99	40	60	1.53	2.0
3[c]	0.5	−40	99	39	61	1.29	1.7
4	0.5	−60	>99	44	56	1.66	1.7
5[c]	0.5	−80	>99	51	49	1.28	1.8
6	1.0	0	83	39	61	1.44	1.6
7	1.0	−20	>99	39	61	2.19	2.4
8[c]	1.0	−40	>99	38	62	2.63	3.0
9[c]	1.0	−60	>99	43	57	3.33	2.2
10[c]	1.0	−80	32	53	47	1.04	1.9

$[\text{NIPAAm}]_0 = 0.5$ mol/l, $[n\text{-Bu}_3\text{B}]_0 = 0.05$ mol/l.
[a] Determined by ^{1}H NMR signals due to methylene group.
[b] Determined by SEC (polystyrene standards).
[c] The monomer, polymer, or both were precipitated during the polymerization reaction.

although the M_ns were smaller than those of the poly (NIPAAm)s obtained in the absence of TMMDP. This result contrasts with a tendency that M_n simply decreased with an increase in the amount of the corresponding monodentate Lewis base, TMP [17].

Fig. 1 shows the relationship between polymerization temperature and *r* diad content of the radically-prepared poly(NIPAAm)s in the absence or presence of TMMDP. In the presence of TMMDP, the isotacticity gradually increased by lowering temperature below −40 °C, although the syndiotacticities of poly(NIPAAm)s obtained at −40–0 °C were higher than those of poly(NIPAAm)s in the absence of TMMDP. Furthermore, the dependence of the stereospecificity on $[\text{TMMDP}]_0$ was hardly observed at lower temperatures and an increase in isotacticity was observed even when an equimolar amount of TMMDP was added at −60 °C. On the other hand, the corresponding monodentate Lewis base, TMP, afforded syndiotactic-rich polymers until −60 °C and an excess amount of TMP was required for an increase in isotacticity of poly(NIPAAm) obtained at −80 °C [17]. These results suggest that bidentate Lewis base has a higher potential of serving for isotactic polymer formation than the corresponding monodentate Lewis base.

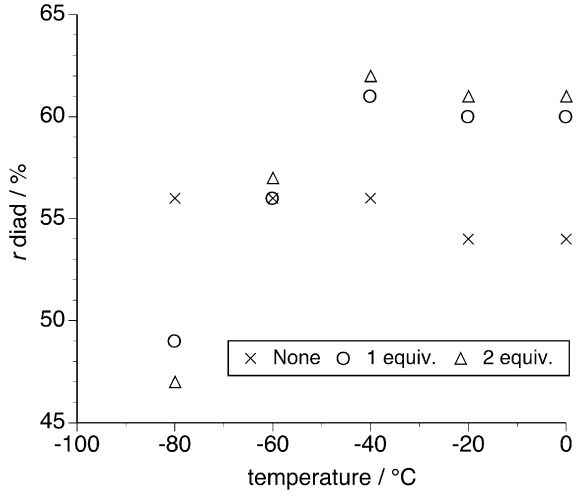


Fig. 3. Relationship between the polymerization temperature and *r* diad content of poly(NIPAAm) prepared in toluene at low temperatures in the presence of T*i*PMDP.

Next, we conducted NIPAAm polymerization in the presence of TEMDP instead of TMMDP (Table 2). Similar tendencies were observed in polymer yield and M_n with the case of TMMDP. Interestingly, an increase in isotacticity was observed only when a twofold amount of TEMDP was added at −80 °C (Fig. 2). Thus, it is suggested that ethyl ester has poor ability to afford isotactic polymers compared with methyl ester. This result corresponds to the results obtained in the presence of the corresponding monodentate Lewis base, triethyl phosphate (TEP) [17].

Thus, we examined the effect of bulkier bidentate Lewis base such as T*i*PMDP on the stereospecificity of NIPAAm polymerization (Table 3). The addition of T*i*PMDP also increased polymer yield and M_n of the obtained poly(NIPAAm)s. The isotacticity gradually increased again with a decrease in polymerization temperature, although the syndiotacticities of poly(NIPAAm)s obtained at −40–0 °C were higher than those of poly(NIPAAm)s in the absence of T*i*PMDP (Fig. 3). The significant induction of isotactic-specificity was observed even by adding an equimolar amount of T*i*PMDP and the induced isotactic-specificity was higher than that in the presence of TMMDP. It is noteworthy that the corresponding monodentate Lewis base, T*i*PP, never afforded isotactic poly(NIPAAm)s even by lowering polymerization temperature to −80 °C [18]. Thus, these results suggested again the high potential of bidentate Lewis base for induction of isotactic-specificity of NIPAAm polymerization.

3.2. Stoichiometry of NIPAAm-TiPMDP complex

As previously reported, the stereospecificity of radical polymerization of the hydrogen-bond-assisted complexed

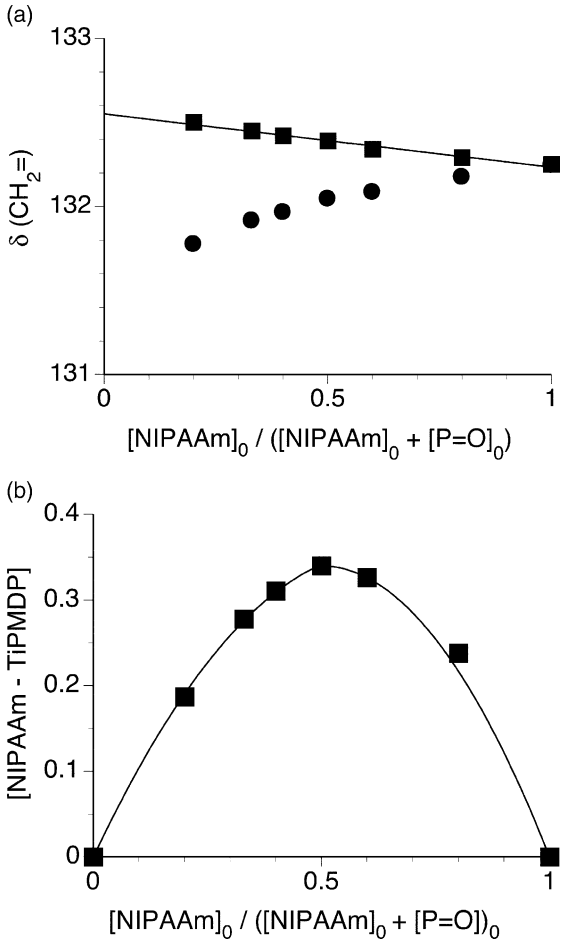


Fig. 4. Job's plots for the association of NIPAAm with T*i*PMDP at 0 °C evaluated from the changes in the methylene carbon chemical shifts of NIPAAm in the presence of T*i*PMDP (■) ($[NIPAAm]_0 + [P=O]_0 = 0.25$ mol/L). (●) denotes chemical shift of NIPAAm alone at the corresponding concentration.

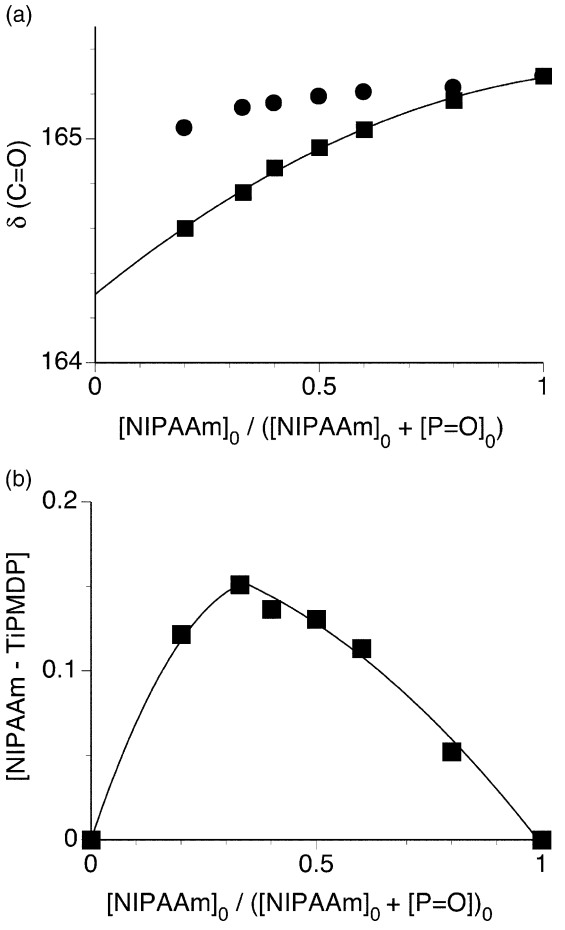


Fig. 5. Job's plots for the association of NIPAAm with T*i*PMDP at −80 °C evaluated from the changes in the carbonyl carbon chemical shifts of NIPAAm in the presence of T*i*PMDP (■) ($[NIPAAm]_0 + [P=O]_0 = 0.25$ mol/L). (●) denotes chemical shift of NIPAAm alone at the corresponding concentration.

NIPAAm strongly depends on the stoichiometry of the complex between NIPAAm and monodentate Lewis base [16–18]. Thus, we conducted ^{13}C NMR analysis under the following conditions ($[NIPAAm]_0 + [P=O]_0 = 0.25$ mol/L, in toluene-d_8 at −80 or 0 °C) to investigate the stoichiometry of the NIPAAm-T*i*PMDP complex [20].

Fig. 4(a) shows changes in the chemical shift of methylene carbon of NIPAAm at 0 °C when the fraction of $[NIPAAm]_0$ was varied. The plots roughly obeyed a linear relationship. Thus, the stoichiometry of the NIPAAm-T*i*PMDP complex was evaluated by Job's method (Fig. 4(b)) with the following Eq. (1); [21]

$$[\text{NIPAAm}-\text{T}i\text{PMDP}] = \frac{\delta(\text{CH}_2=)-\delta(\text{CH}_2=)_f}{\delta(\text{CH}_2=)-\delta(\text{CH}_2=)_f}\times[\text{NIPAAm}]_0 \quad (1)$$

where $\delta(CH_2=)$ and $\delta(CH_2=)_f$ are the chemical shifts of methylene carbon of the sample mixture and NIPAAm alone, respectively. The chemical shift of NIPAAm alone also varied with the concentration (Fig. 4(a)), since NIPAAm itself also associated 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 a linear dependence in Fig. 4(a), because the saturation should be independent of NIPAAm concentration. The maximum was observed at 0.5 of the $[NIPAAm]_0$ fraction (Fig. 4(b)). This means that T*i*PMDP forms hydrogen-bond-assisted complex with NIPAAm at 0 °C at the ratio of [CONH]: [P=O] = 1: 1. It is consistent with the 1:1 complex formation between NIPAAm and monodentate Lewis base, such as phosphoric acid derivatives, at 0 °C [15,17].

Then, we also performed ^{13}C NMR analysis 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 methylene carbon was too small. Thus, we applied the chemical shift of carbonyl carbon to Job's plots to evaluate the stoichiometry at −80 °C. Fig. 5(a) demonstrates changes in the chemical shift of carbonyl carbon of NIPAAm in the presence of T*i*PMDP ($[NIPAAm]_0 + [P=O]_0 = 0.25$ mol/L) and of NIPAAm alone at the corresponding concentration [20]. The chemical shift was

significantly shifted to up-field with the decrease in $[NIPAAm]_0$ in the presence of T*i*PMDP compared with in the absence of T*i*PMDP. The plots roughly obeyed not a linear equation but a quadratic equation. Thus, the chemical shift for the saturated mixture ($\delta(C{=}O)_c$) was calculated from the intercept of a quadratic dependence in Fig. 5(a). Unlike at 0 °C, the maximum was observed around 0.33 of the $[NIPAAm]_0$ fraction (Fig. 5(b)). This means that T*i*PMDP forms hydrogen-bond-assisted complex with NIPAAm at −80 °C at the ratio of [CONH]: [P=O] = 1: 2, although the corresponding monodentate Lewis base, T*i*PP, predominantly formed 1:1 complex with NIPAAm even at −80 °C [18]. If one NIPAAm monomer formed the complex with two T*i*PMDP molecules, the stereospecificity at −80 °C should strongly depend on the ratio of $[TiPMDP]_0/[NIPAAm]_0$. However, the dependence of the stereospecificity on $[TiPMDP]_0/[NIPAAm]_0$ was hardly observed (Fig. 3). Thus, it is assumed that NIPAAm and T*i*PMDP form a chelate complex as expected.

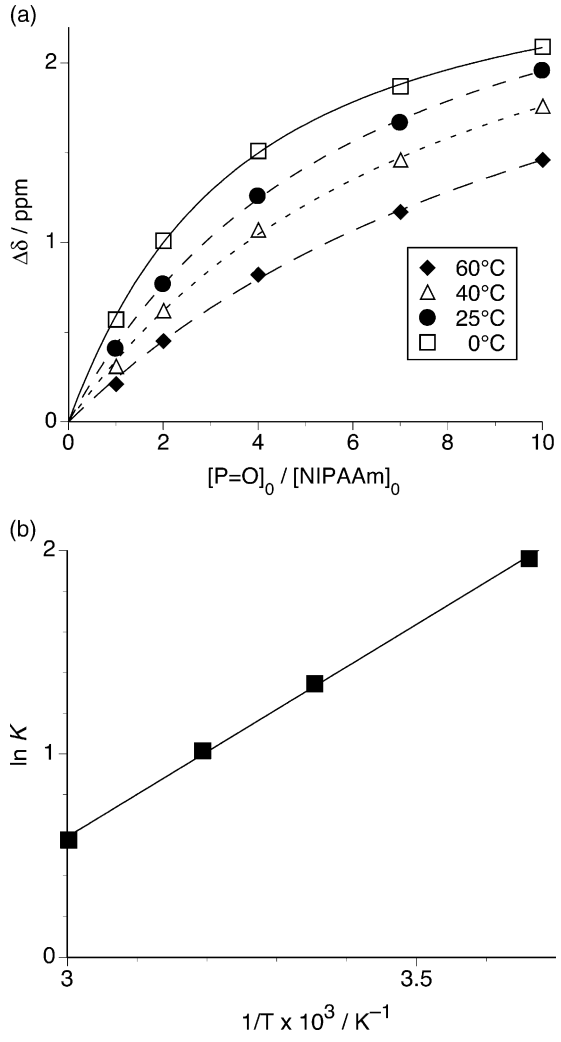
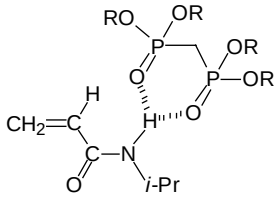


Fig. 6. (a) Changes in the chemical shift of the amide proton of NIPAAm in toluene-d_8 at various temperatures and (b) van't Hoff's plots for equilibrium constants of the mono-binding complex between NIPAAm and T*i*PMDP.



3.3. Equilibrium constant for the mono-binding complex between NIPAAm and TiPMPD

As mentioned above, it was found that NIPAAm and T*i*PMDP form the mono-binding complex at 0 °C as well as NIPAAm and monodentate Lewis bases. Thus, the equilibrium constants (K_1) of the mono-binding complex (Scheme 1) at 0–60 °C were determined by changes in the chemical shift of amide proton of NIPAAm, on the assumption that NIPAAm and T*i*PMDP form the mono-binding complex above 0 °C. Fig. 6(a) demonstrates the relationship between the change in the chemical shift and the ratio of $[P{=}O]_0/[NIPAAm]_0$ with the constant concentration of $[NIPAAm]_0$ (5.0×10^{-2} mol/L) in toluene-d_8 at several temperatures [20]. The equilibrium constants (K_1) (Table 4) were determined by the analysis of the data in Fig. 6(a) by a nonlinear least-squares fitting to the following equation (2): [22]

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

$$b = 1 + X + \frac{1}{(K_1[NIPAAm]_0)}$$

$$X = \frac{[P=O]_0}{[NIPAAm]_0}$$

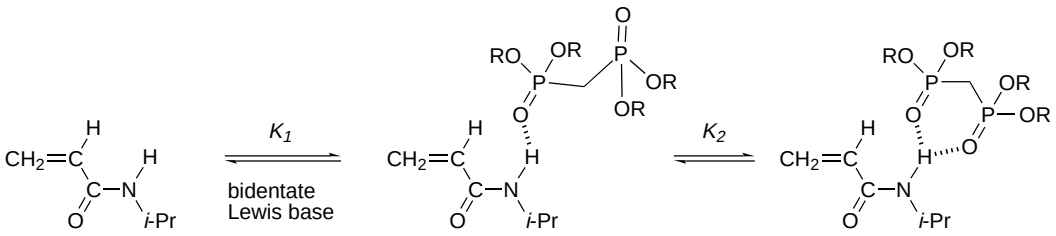
where $\Delta\delta$ and $\Delta\delta'$ are the changes in the chemical shift of amide proton of NIPAAm for the given solution and a saturated solution, respectively. The K_1 values were smaller than those for the 1:1 complexes of NIPAAm and HMPA [16], but comparable to those for the 1:1 complexes of NIPAAm and phosphates [17,18]. Thus, it is assumed that the phosphoryl groups in T*i*PMDP have basicity corresponding to those of phosphates.

The enthalpy (ΔH) and the entropy (ΔS) for the complex formation were determined to be -17.4 ± 0.4 kJ/mol and -47 ± 1 J/mol K, respectively, from the van't Hoff's plots

Table 4
Equilibrium constants (K_1) of the mono-binding complex between NIPAAm and T*i*PMDP

Temperature (°C)	K_1 (l/mol)
60	1.78
40	2.76
25	3.84
0	7.10

Determined by ^{1}H NMR signals due to amide proton ($[NIPAAm]_0 = 5.0\times10^{-2}$ mol/l, toluene-d_8).



Scheme 1. Stepwise formation of the chelate complex via the mono-binding complex.

(Fig. 6(b)) using the following Eq. (3):

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{3}$$

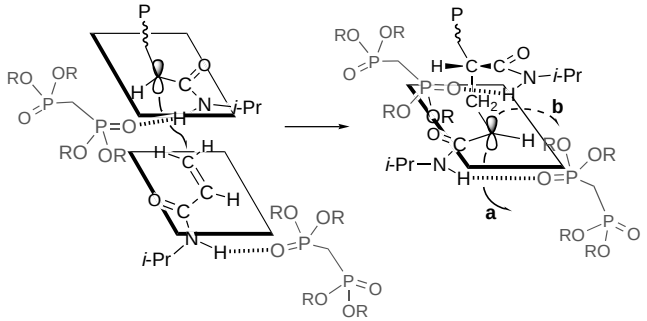
where R is a gas constant (8.315 J/mol K) and T is the absolute temperature (K). These values were also comparable to those for the NIPAAm-phosphate complexes.

3.4. Mechanistic speculation on stoichiometry of the NIPAAm complex with bidentate Lewis base

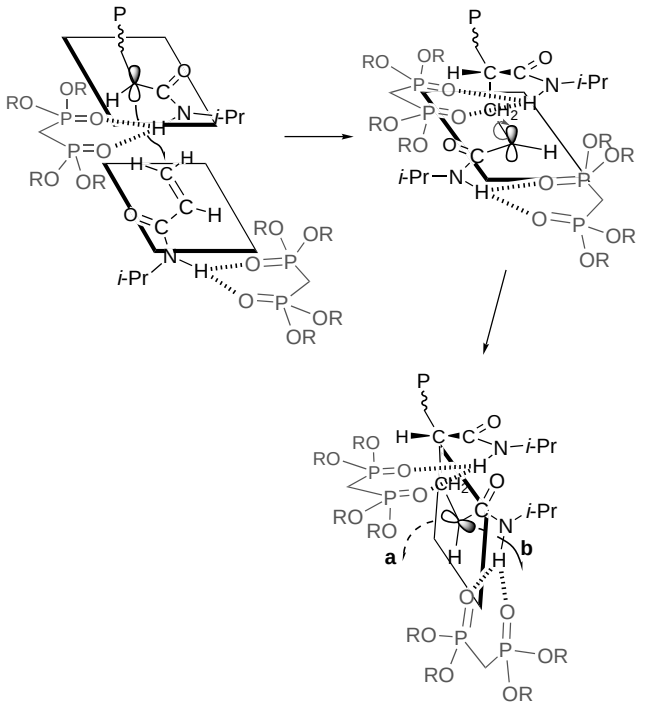
Syndiotactic-rich poly(NIPAAm)s were obtained at −40–0 °C in the presence of any methylenebisphosphonates. The NMR analysis of the mixture of NIPAAm and T*i*PMDP revealed that T*i*PMDP coordinated to NIPAAm using one phosphoryl group at 0 °C. These results correspond to the results observed for a combination of NIPAAm and monodentate Lewis base at 0 °C. Thus, it is thought that the syndiotactic-specificity was induced in the same manner as that induced by phosphoric acid derivatives [16,17] as follows: (1) methylenediphosphonates behaved as a monodentate Lewis base, (2) a propagating radical approached a monomer, as shown in Scheme 2, to reduce the steric repulsion between the Lewis base coordinating to the propagating radical and that coordinating to the incoming monomer, (3) Lewis base coordinating to the penultimate monomeric unit of the newly formed propagating radical suppressed a rotation of the single bond near the chain-end by the steric interaction with the amide group at the chain-end monomeric unit, and (4) the Lweis base coordinating to the penultimate monomeric unit also limited an approach by the next incoming monomer via the pathway **b** that affords *meso* diad. As a result, the formation of polymers rich in syndiotacticity was favored.

On the other hand, the increase in isotacticcity was observed for poly(NIPAAm)s obtained at −80 °C in the presence of TMMDP and T*i*PMDP. Although NIPAAm and T*i*PP predominantly formed 1:1 complex even at −80 °C, it was revealed that NIPAAm and T*i*PMDP formed a chelate complex at −80 °C, probably because of a significant chelate effect in addition to slightly less bulkiness of T*i*PMDP compared with two molecules of T*i*PP. The structure of the chelate complex correspond to that of the 1:2 complex observed for a combination of NIPAAm and primary alkyl phosphates at −80 °C. Thus, it is suggested that the isotactic-specificity was also induced in the same manner as that induced by primary alkyl phosphates [17] as follows: (1) methylenediphosphonates behaved as a bidentate Lewis base, (2) a complexed propagating radical approached a complexed monomer as shown in Scheme 3 to reduce the steric repulsion, (3) a chelate coordination, however, made the environment around the newly formed propagating chain-end crowdedly more than the situation when the bidentate Lewis base coordinated with one phosphoryl group, (4) thus the propagating radical conformationally changed to reduce the extreme hindrance due to the bidentate Lewis bases coordinating to the penultimate and chain-end monomeric units, and (5) the Lewis base coordinating to the penultimate monomeric unit prevented the propagating radical from the next propagation via the pathway **a** that affords *racemo* diad. Consequently, an increase in isotacticity was observed.

It appeared that isotacticity of poly(NIPAAm) obtained at −80 °C in the presence of TEMDP was smaller than that in the presence of TMMDP. Similar result was observed when monodentate Lewis base was added; TEP induced less isotactic-specificity at −80 °C than TMP, although the equilibrium constant for 1:1 NIPAAm-TEP complex at 0 °C was larger than that for 1:1 NIPAAm-TMP complex [17]. Thus, it is not that NIPAAm monomer should just be strongly coordinated by Lewis base in order to propagate isotactic-specifically, because, for the formation of the chelate complex, the second phosphoryl group requires a sufficient space around the amide hydrogen coordinated by the first phosphoryl group (Scheme 1).



Scheme 2. Proposed mechanism for the syndiotactic-specific propagation induced by methylenediphosphonates behaving as a monodentate Lewis base.



Scheme 3. Proposed mechanism for the isotactic-specific propagation induced by methylenediphosphonates behaving as a bidentate Lewis base.

4. Conclusions

Radical polymerization of NIPAAm was investigated in the presence of methylenediphosphonates as bidentate Lewis bases. The increase in the isotacticity was observed for poly(NIPAAm)s obtained at −80 °C in the presence of equimolar amounts of TMMDP and T*i*PMDP, whereas syndiotactic-rich poly(NIPAAm)s were obtained at −40–0 °C in the presence of any bidentate Lewis base. NMR analysis revealed that NIPAAm and T*i*PMDP formed a chelate complex at −80 °C, whereas mono-binding complex was predominantly formed at 0 °C. Thus, it was demonstrated that the complexation mode of bidentate Lewis base was one of the most important factors for decision of stereospecificity of NIPAAm polymerization; the mono-binding complex favored a syndiotactic-specific propagation and the chelate complex favored an isotactic-specific propagation. This corresponds with the dependence of stereospecificity of NIPAAm polymerization on the stoichiometry of the complex between NIPAAm and monodentate Lewis base. Furthermore, T*i*PMDP afforded isotactic-rich poly(NIPAAm)s at −80 °C, whereas the corresponding monodentate Lewis base, T*i*PP, produced syndiotactic-rich poly(NIPAAm)s regardless of temperature. These results evidenced that bidentate Lewis base had higher potential for induction of isotactic-specificity of NIPAAm polymerization than monodentate Lewis base. Further work is now under way to examine effect of the linker length between two phosphoryl groups on the stereospecificity of NIPAAm polymerization.

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