Direct Synthesis of Syndiotactic-rich Poly(*N*-isopropylacrylamide) via Radical Polymerization of Hydrogen-Bond-Complexed Monomer

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Abstract

Radical polymerization of *N*-isopropylacrylamide (NIPAAm) in toluene was investigated in the presence of hexamethylphosphoramide (HMPA). We succeeded in directly preparing syndiotactic-rich poly(NIPAAm), the syndiotacticity of which (r = 70%) is the highest among those of radically-prepared poly(NIPAAm)s so far reported, by lowering polymerization temperature to –60°C in the presence of a twofold amount of HMPA. The NMR analysis revealed that the induced syndiotactic-specificity was ascribed to 1:1 complex formation between NIPAAm and HMPA. Furthermore, thermodynamic analysis described that the induced syndiotactic-specificity was enthalpically achieved.

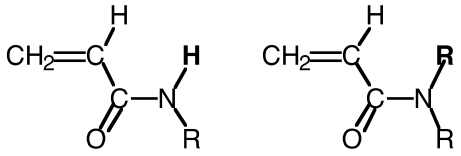
Keywords: *N*-isopropylacrylamide, radical polymerization, stereospecific polymerization, syndiotactic polymer, hydrogen bond, NMR

1. Introduction

Poly(*N*-isopropylacrylamide) [poly(NIPAAm)] has been widely investigated as

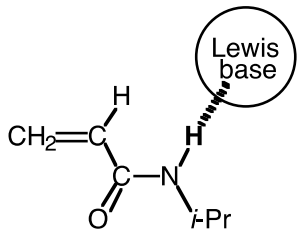
a switching device, since poly(NIPAAm) shows a lower critical solution temperature (LCST) that lies between 30 and 35°C [1-4]. To control the LCST, many researchers investigated radical copolymerization of NIPAAm, since the LCST depends on the microstructure including a copolymer composition. However, although the stereostructure of macromolecules also significantly influences polymer properties, there are limited reports on a stereoregularity of poly(NIPAAm) [5-7] due to the following reasons; 1) *N*-isopropylacrylamide (NIPAAm) dose not undergo a vinyl polymerization via an anionic mechanism, which is an effective method for the stereocontrol of a vinyl polymerization, due to the acidic amide proton and 2) hence poly(NIPAAm) is usually prepared by a radical polymerization.

In general, radical polymerization of *N*-monosubstituted acrylamides gives atactic polymers regardless of polymerization conditions such as polymerization temperature and solvent, except for isotactic-specific polymerization in the presence of Lewis acids such as yttrium trifluoromethanesulfonate [7]. Several stereocontrols, however, have been reported for radical polymerization of *N*,*N*-disubstituted acrylamides in spite of the high activity of electrically neutral propagating species [8,9]. *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 [10]. Thus, it is assumed that the steric interaction of the second substituent is very important for controlling the stereospecificity of radical polymerization of acrylamide derivatives.



A hydrogen bond plays an important role in determining the three-dimensional structure of supramolecular self-assembly in natural and unnatural systems [11-13]. However, there are limited reports on the control of polymerization reactions of vinyl monomers with a hydrogen-bonding interaction [14-19]. Recently, we found that radical polymerization of NIPAAm, one of *N*-monosubstituted acrylamides, in toluene at

0°C in the presence of a twofold amount of hexamethylphosphoramide (HMPA) afforded syndiotactic-rich poly(NIPAAm) with *racemo* (*r*) diad of 63% [20]. In addition, we found that the stereocontrol from syndiotactic-rich to isotactic-rich could be achieved by changing the polymerization temperature in the presence of a fourfold amount of primary alkyl phosphates instead of HMPA [21]. For instance, syndiotactic-rich poly(NIPAAm) with *r* diad of 65% was obtained in the presence of triethyl phosphate at –40°C and the use of tri-*n*-butyl phosphate (TBP) at –80°C provided isotactic-rich poly(NIPAAm) with *meso* (*m*) diad of 57%. The NMR analyses of mixtures of NIPAAm and phosphoric acid derivatives revealed that NIPAAm and the added Lewis base formed complex through a hydrogen-bonding interaction [20,21]. Thus, it is assumed that the coordinating Lewis base behaved like the second substituent at the nitrogen amide atom and hence the direct stereocontrol of NIPAAm polymerization was achieved.



In this study, the NIPAAm polymerization in the presence of HMPA was investigated in more detail by changing the polymerization conditions including polymerization temperature and the ratio of $[HMPA]_0/[NIPAAm]_0$. Then, it was found that lowering temperature was very efficient in increasing syndiotactic-specificity of NIPAAm polymerization and syndiotactic-rich poly(NIPAAm) with *r* diad = 70% was obtained at –60°C in the presence of a twofold amount of HMPA.

2. Experimental Section

2.1 Materials

N-Isopropylacrylamide (NIPAAm) was recrystallized from hexane-benzene mixture. Dimethyl 2,2'-azobisisobutyrate (MAIB) and 1,1'-azobis(cyclohexanecarbonitrile) (ACN) were recrystallized from methanol. 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 (1.0M), hexamethylphosphoramide (HMPA), and 2,2'-azobis(2,4-dimethylvaleronitrile) (AVN) were commercially obtained and used without further purification for polymerization reaction.

2.2 Polymerization

Typical polymerization procedure is as follows; NIPAAm (0.628 g, 5.5 mmol) was dissolved in toluene to prepare the 5 mL solution of 1.1 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 (0.44 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 mixtures (9 : 1 v/v), and the precipitated polymer was collected by filtration, 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 ^{1}H and ^{13}C NMR spectra of NIPAAm monomer, HMPA, or both were measured in toluene-d_8 at the desired temperatures 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.

3. Results and discussion

3.1 Tacticity dependence on polymerization temperature and amount of the added HMPA

Table 1 summarizes the results of radical polymerization of NIPAAm in the

<Table 1>

absence or presence of HMPA at the temperature range from –80°C to 80°C. In the absence of HMPA, monomer and polymer were precipitated during the polymerization reaction at low temperatures, probably due to the low solubility in toluene. Thus, polymer yield decreased as the polymerization temperature decreased. However, the addition of HMPA improved the solubility of both monomer and polymer through a coordination so that poly(NIPAAm)s were obtained at high yields even at low temperatures. The addition of HMPA also affected number average molecular weight (M_n) and molecular weight distribution (M_w/M_n), and both decreased with increasing the amount of the added HMPA.

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

<Fig. 1>

HMPA. No significant effect was observed in tacticities of the poly(NIPAAm)s obtained in the absence of HMPA, although the tacticity was slightly scattered at low temperatures, probably because NIPAAm monomer and poly(NIPAAm) were insoluble in toluene without HMPA. However, syndiotacticity of poly(NIPAAm) prepared in the presence of an equimolar amount of HMPA with NIPAAm monomer increased linearly

as the polymerization temperature was lowered. The maximum of r = 65% was observed between –60 and –40°C. Furthermore, a twofold amount of HMPA enhanced the syndiotactic-specificity and shifted the maximum point to a lower temperature. Poly(NIPAAm) with 70% of *r* diad was obtained at –60°C. The syndiotacticity of 70% is the highest among those of radically-prepared poly(NIPAAm)s so far reported. However, further lowering the temperature decreased the syndiotacticity of the obtained poly(NIPPAm)s regardless of the amount of the added HMPA.

Fig. 2 shows ^{1}H NMR spectra of main-chain methine and methylene groups of poly(NIPAAm)s prepared at 60°C without HMPA and at –60°C with a twofold amount of HMPA. It is confirmed that the latter obviously displayed sharper and more stereoregulated signals than the former.

<Fig. 2>

3.2 Stoichiometry of NIPAAm-HMPA complex

In the previous paper [21], we reported that NIPAAm and TBP form 1:1 complex at 0°C, where syndiotactic-rich poly(NIPAAm)s were obtained, and formed predominantly 1:2 complex at –80°C, where isotactic-rich poly(NIPAAm)s were obtained. Thus, it is assumed that the stereospecificity strongly depends on the stoichiometry of NIPAAm-Lewis base complex.

The syndiotacticity of the obtained poly(NIPAAm)s decreased at lower temperature than –60°C, although the syndiotactic-specificity was enhanced by lowering temperature until –60°C. It is possible that the change in the stoichiometry of NIPAAm-HMPA complex attributes to the reduced syndiotactic-specificity at lower temperatures, because NIPAAm and HMPA also form 1:1 complex at 0°C [20]. Thus, we conducted ^{13}C NMR analysis under the following conditions ($[NIPAAm]_0 + [HMPA]_0 = 0.25$ mol/L, in toluene-d_8 at –80°C) to investigate the stoichiometry of the NIPAAm-HMPA complex

at lower temperature.

Fig. 3 shows changes in the chemical shift of carbonyl carbon of NIPAAm at –80°C when the fraction of $[NIPAAm]_0$ was varied. The plots roughly obeyed a

<Fig. 3>

quadratic equation, whereas those for 0°C displayed a rough linear dependence [20]. Thus, the stoichiometry of the complex was evaluated by Job's method (Fig. 4) with the following eq. (1); [22]

$$[\text{NIPAAm - HMPA}] = \frac{\delta\,(C{=}O) - \delta\,(C{=}O)_f}{\delta\,(C{=}O)_c - \delta\,(C{=}O)_f} \times [\text{NIPAAm}]_0 \quad (1)$$

where $\delta(C{=}O)$ and $\delta(C{=}O)_f$ are the chemical shifts of carbonyl carbon of the sample mixture and NIPAAm alone, respectively. As previously reported, [20,21] the

<Fig. 4>

chemical shift of NIPAAm alone also varied with the concentration (Fig. 3), since 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 $\delta(C{=}O)_f$. The chemical shift for the saturated mixture ($\delta(C{=}O)_c$) was calculated from the intercept of a quadratic dependence in Fig. 3, since the saturation should be independent of NIPAAm concentration. The maximum was observed at 0.5 of the $[NIPAAm]_0$ fraction (Fig. 4). This means that HMPA forms 1:1 complex with NIPAAm even at –80°C, unlike TBP. Thus, it is suggested that the decrease in the syndiotactic-specificity at temperatures lower than –60°C is attributable to another mechanism, although the details are not clear at this time.

3.3 Equilibrium constant for NIPAAm-HMPA complex.

The equilibrium constant (K) of the NIPAAm-HMPA complex was determined by changes in the ^{1}H NMR chemical shift of amide proton of NIPAAm. Fig. 5 demonstrates the relationship between the change in the chemical shift and the

<Fig. 5>

ratio of $[HMPA]_0/[NIPAAm]_0$ 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 Fig. 5 by a nonlinear

<Table 2>

least-squares fitting to the following equation (2): [23]

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

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

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

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 values below 0°C were not obtained, because the changes in the chemical shift of amide proton of NIPAAm were too small to evaluate the constants. Thus, we performed van't Hoff's plots for the obtained K values as shown in Fig. 6.

<Fig. 6>

The enthalpy (ΔH) and the entropy (ΔS) for the complex formation were determined to be $-(2.67 \pm 0.12) \times 10^2$ J/mol and $-(5.2 \pm 0.4) \times 10^{-1}$ J/mol•K, respectively, from the

following equation (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). Thus, we calculated the K values for –60 to –20°C, on the assumption that ΔH is constant from –60°C to 60°C, and summarized the calculated values in Table 2 with the obtained values for 0°C to 60°C.

By applying the K values to the polymerization conditions, we evaluated the degree of association (α) of NIPAAm as summarized in Table 2. When an equimolar amount of HMPA was added, only 73% of NIPAAm formed the complex at 60°C and the α value increased until 95% by lowering temperature to –60°C. However, when a twofold amount of HMPA was added, only 5% of NIPAAm was free even at 60°C and NIPAAm formed the complex quantitatively at –60°C. Thus, this result reconfirmed that the 1:1 complex formation was the key to the induced syndiotactic-specificity.

3.4 The role of HMPA estimated from the viewpoint of thermodynamics.

The syndiotacticity of the poly(NIPAAm)s obtained in the presence of HMPA linearly increased as the polymerization temperature was lowered until –40°C (HMPA = 1 equiv.) or until –60°C (HMPA = 2 equiv.). Thus, we conducted Fordham's plots [24] for NIPAAm polymerizations in the absence or presence of HMPA in the appropriate temperature range (Fig. 7). The (apparent) differences in activation enthalpy ($\Delta H^{\ddagger}$)

<Fig. 7>

and the (apparent) differences in activation entropy ($\Delta S^{\ddagger}$) between isotactic and syndiotactic propagations were determined by the linear dependences according to the following equation (4):

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

where *Pi* and *Ps* denote the mole fractions of isotactic and syndiotactic diads, respectively. In Table 3, the obtained values are summarized. Both the $\Delta Hi^{\ddagger}$ - $\Delta Hs^{\ddagger}$ and the $\Delta Si^{\ddagger}$ - $\Delta Ss^{\ddagger}$ were very small for the polymerization in the absence of HMPA.

<Table 3>

However, the addition of HMPA drastically increased the apparent differences in activation enthalpy, suggesting that the syndiotactic-specific propagation in this polymerization system was enthalpically favored. This is consistent with the results observed in syndiotactic-specific radical polymerization of *N*,*N*-diphenylacrylamide [9]. Thus, it is suggested that the syndiotactic-specificity was educed by the coordinating HMPA behaving like the second substituent at the nitrogen amide atom, as expected.

On the other hand, the negative $\Delta Si^{\ddagger}$ - $\Delta Ss^{\ddagger}$ was changed to positive values by adding HMPA, although the absolute values were kept small. It is suggested that the syndiotactic-specificity in this polymerization system was entropically disfavored. In the previous paper [21], we proposed the mechanism of the educed syndiotactic-specific propagation as follows (Scheme 1):

<Scheme 1>

(1) the single bond near the propagating chain-end can rotate freely to reduce the steric repulsion between the bulkier substituents, the amide groups, at the penultimate and chain-end monomeric units,
(2) the conformationally rotated radicals react with a new incoming monomer via two possible pathways (pathway **a** should form an *r* diad and pathway **b** should form an *m* diad) and thus atactic poly(NIPAAm)s are obtained in the absence of HMPA,
(3) the rotation of the single bond near the propagating chain-end, however, is limited

because of the steric hindrance between the HMPA at the penultimate monomeric unit and the amide group at the chain-end monomeric unit, although the bulky HMPAs coordinate to both the penultimate and the chain-end monomeric units,

(4) the steric hindrance of the HMPA coordinating to the penultimate monomeric unit also limits the approach via pathway **b** by the next incoming monomer that is also coordinated with HPMA and thus syndiotactic-rich poly(NIPAAm)s are formed in the presence of HMPA.

Thus, the positive $\Delta Si^{\ddagger}$ - $\Delta Ss^{\ddagger}$ means that our proposed mechanism is thermodynamically supported, because the syndiotactic-specific propagation is based on the fixation of the conformation near the propagating chain-end in this mechanism.

4. Conclusions

We succeeded the direct synthesis of syndiotactic-rich poly(NIPAAm)s utilizing a hydrogen-bond-assisted complex formation. The diad syndiotacticity reached 70% by lowering polymerization temperature to –60°C in the presence of a twofold amount of HMPA, although it is not clear at this time why further decrease in polymerization temperature reduces the syndiotactic-specificity. The syndiotacticity (r = 70%) is the highest among those of radically-prepared poly(NIPAAm)s so far reported. Thus, we can conclude that even a weak hydrogen-bonding interaction is significantly available for the stereocontrol of radical polymerizations of *N*-monosubstituted acrylamides, taking into consideration that poly(NIPAAm) with 77% syndiotactic diad was prepared even by an anionic polymerization of NIPAAm, the acidic proton of which was protected [6]. Now, further work is under way to extend the present results to higher level of stereoregulation as well as to reveal the reason why the syndiotactic-specificity reduced at polymerization temperature lower than –60°C.

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

Temp.	Initiator	HMPA	Yield	Diad tacticity/%[b]		M_n[c]	M_w/M_n[c]
		mol/l	%	*m*	*r*	$\times 10^4$	
80	ACN	0.0	>99	44	56	8.58	3.0
80	ACN	1.0	>99	43	57	2.10	1.9
80	ACN	2.0	94	42	58	1.14	1.8
60	MAIB	0.0	>99	45	55	11.6	2.4
60	MAIB	1.0	98	41	59	2.3	2.1
60	MAIB	2.0	95	40	60	1.37	1.8
40	AVN	0.0	88	45	55	15.8	2.0
40	AVN	1.0	71	40	60	3.82	1.9
40	AVN	2.0	62	39	61	2.35	1.6
0[d]	*n*-Bu_3B	0.0	>99	45	55	6.96	1.9
0	*n*-Bu_3B	1.0	>99	38	62	1.27	1.6
0	*n*-Bu_3B	2.0	98	37	63	0.91	1.6
–20[d]	*n*-Bu_3B	0.0	56	45	55	3.41	2.3
–20	*n*-Bu_3B	1.0	>99	36	64	1.07	1.8
–20	*n*-Bu_3B	2.0	>99	34	66	0.97	1.7
–40[d]	*n*-Bu_3B	0.0	84	44	56	1.57	2.0
–40	*n*-Bu_3B	1.0	>99	35	65	1.28	2.6
–40	*n*-Bu_3B	2.0	99	32	68	1.30	2.2
–50[d]	*n*-Bu_3B	0.0	63	44	56	1.42	2.2
–50	*n*-Bu_3B	1.0	>99	35	65	0.91	1.7
–50	*n*-Bu_3B	2.0	>99	31	69	0.85	1.6
–60[d]	*n*-Bu_3B	0.0	10	43	57	0.74	1.8
–60	*n*-Bu_3B	1.0	>99	35	65	1.18	1.9
–60	*n*-Bu_3B	2.0	>99	30	70	1.02	1.9
–70[d]	*n*-Bu_3B	0.0	96	45	55	4.18	1.6
–70	*n*-Bu_3B	1.0	>99	37	63	1.42	1.7
–70	*n*-Bu_3B	2.0	>99	33	67	1.11	1.8
–80[d]	*n*-Bu_3B	0.0	18	44	56	1.11	3.5
–80	*n*-Bu_3B	1.0	87	39	61	1.16	1.6
–80	*n*-Bu_3B	2.0	86	36	64	1.25	1.6

a. $[NIPAAm]_0 = 1.0$ mol/l, $[Initiator]_0 = 5.0 \times 10^{-2}$ mol/l (40 ~ 80°C), $[n\text{-}Bu_3B]_0 = 0.1$ mol/l (–80 ~ 0°C).

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

c. Determined by SEC (polystyrene standards).

d. Monomer and/or polymer were precipitated during the polymerization reaction.

Table 2

Equilibrium constants (K) for the interaction between NIPAAm and HMPA and degree of association (α) in the polymerization system[a]

Temperature	K	α[b]	
°C	L/mol	HMPA = 1 equiv.	HMPA = 2 equiv.
60	10.1	0.73	0.92
40	16.5	0.78	0.95
25	23.9	0.82	0.96
0	44.0	0.86	0.98
–20	(86.1)[c]	0.90	0.99
–40	(183)[c]	0.93	0.99
–60	(446)[c]	0.95	1.00

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

b. Calculated with $[NIPAAm]_0 = 1.0$ mol/l.

c. Calculated from van't Hoff relationship.

Table 3
(Apparent) activation parameters for NIPAAm polymerization in the absence or presence of HMPA

HMPA	$\Delta Hi^{\ddagger}$ - $\Delta Hs^{\ddagger}$ J / mol	$\Delta Si^{\ddagger}$ - $\Delta Ss^{\ddagger}$ J / mol•K
None	1.7 ± 1.3	$-(2.1 \pm 0.5) \times 10^{-2}$
1 equiv.	26.8 ± 2.0	$(3.9 \pm 0.7) \times 10^{-2}$
2 equiv.	33.5 ± 1.3	$(5.4 \pm 0.5) \times 10^{-2}$

Captions for Fig.s and Scheme

Fig. 1. The dependence of *r* diad in poly(NIPAAm)s prepared in toluene on both polymerization temperature and amount of the added HMPA.

Fig. 2. Expanded ^{1}H NMR spectra of main-chain methine and methylene groups of poly(NIPAAm)s prepared (a) at 60°C without HMPA and (b) at –60°C with a twofold amount of HMPA. Measured in DMSO-d_6 at 150°C. *: hexane.

Fig. 3. Changes in the carbonyl carbon chemical shifts of NIPAAm in the presence of HMPA (■) ($[NIPAAm]_0 + [HMPA]_0 = 0.25$ mol/L) and of NIPAAm alone at the corresponding concentration (●), measured in toluene-d_8 at –80°C.

Fig. 4. Job's plots for the association of HMPA with NIPAAm at –80°C evaluated from the changes in the chemical shift of carbonyl carbon of NIPAAm.

Fig. 5. Changes in the chemical shift of the amide proton of NIPAAm in the presence of HMPA, in toluene-d_8 at various temperatures.

Fig. 6. van't Hoff's plots for the 1:1 complexation of NIPAAm and HMPA in toluene-d_8.

Fig. 7. Fordham's plots for polymerization of NIPAAm in the absence or presence of HMPA.

Scheme 1. Proposed mechanism for the syndiotactic-specific propagation induced by the coordination of HMPA.

Fig. 1 / T. Hirano et al.

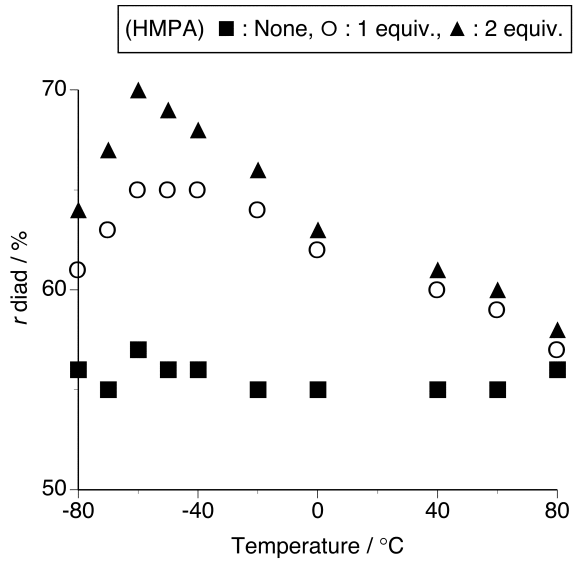


Fig. 2 / T. Hirano et al.

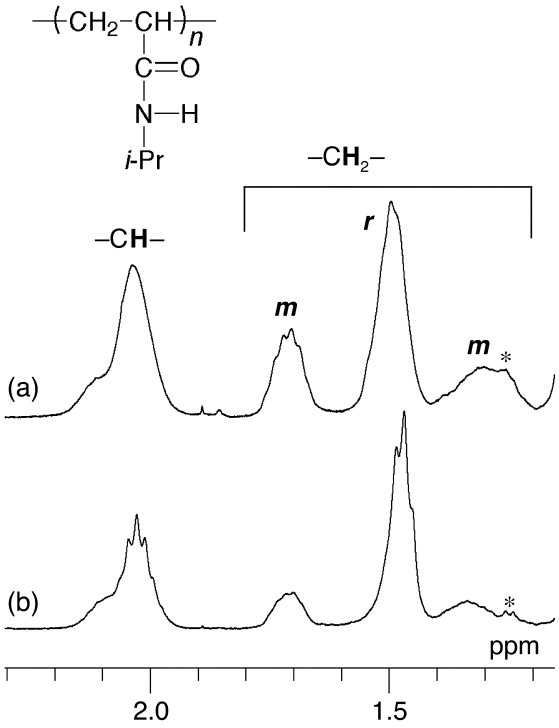


Fig. 3 / T. Hirano et al.

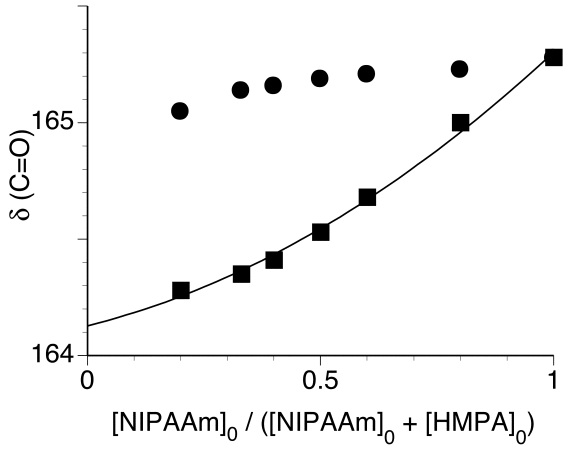


Fig. 4 / T. Hirano et al.

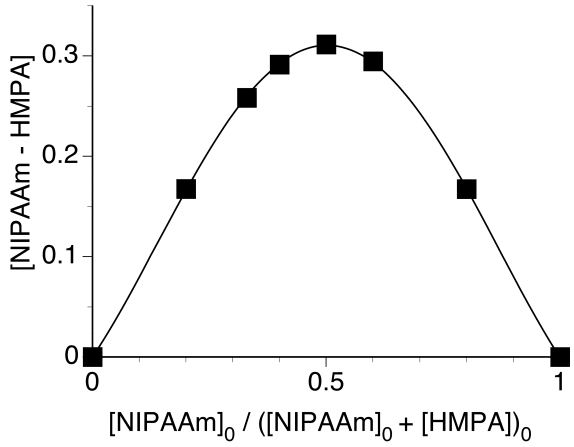


Fig. 5 / T. Hirano et al.

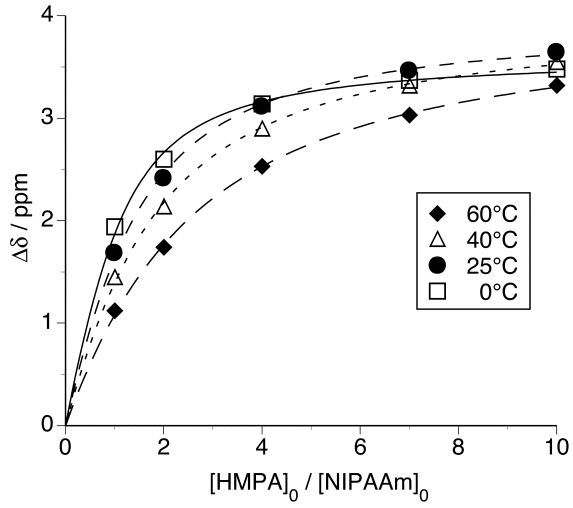


Fig. 6 / T. Hirano et al.

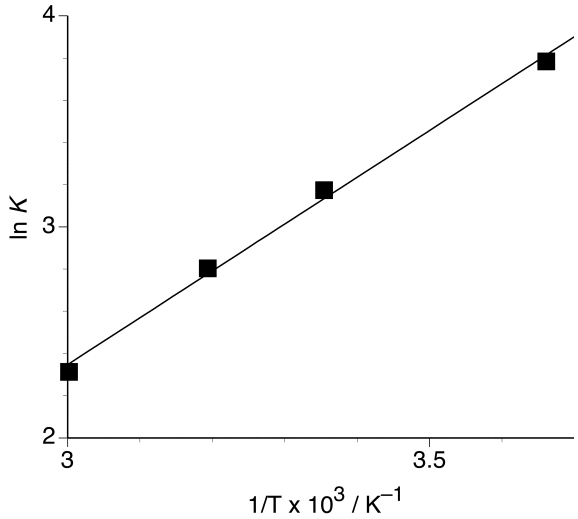
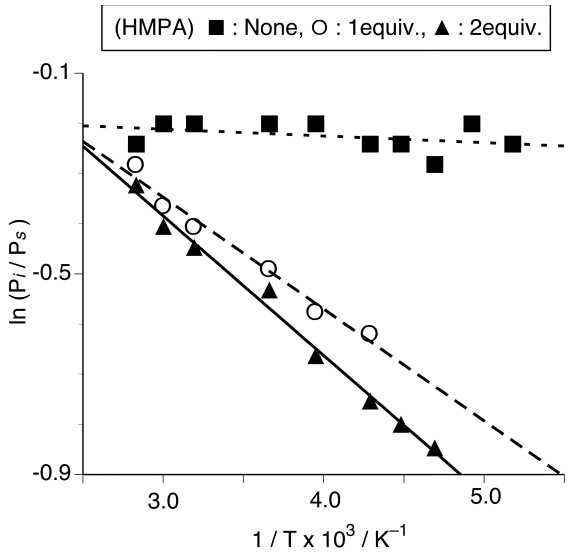


Fig. 7 / T. Hirano et al.



Scheme 1 / T. Hirano et al.