Effect of a combination of hexamethylphosphoramide and alkyl alcohol on the stereospecificity of radical polymerization of *N*-isopropylacrylamide

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ABSTRACT

Radical polymerization of *N*-isopropylacrylamide (NIPAAm) was investigated at low temperatures in the presence of both hexamethylphosphoramide (HMPA) and alkyl alcohols. Although HMPA and alkyl alcohols separately induced syndiotactic specificity in NIPAAm polymerization in toluene at low temperatures, a combination of HMPA and less bulky alkyl alcohols, such as methanol and ethanol, was found to induce isotactic specificity at –80°C. NMR analysis of mixtures of NIPAAm, ethanol and HMPA suggested the formation of a 1:1:1 complex through O–H•••O=C and N–H•••O=P hydrogen bonding. It is believed that the steric effect of HMPA enhanced by cooperative hydrogen bonding was responsible for the combined effect of HMPA and alkyl alcohols in inducing isotactic specificity.

Keywords: hydrogen bonding; *N*-isopropylacrylamide; stereospecific radical polymerization

1. Introduction

We have reported stereospecific radical polymerization of *N*-isopropylacrylamide (NIPAAm) via complex formation of NIPAAm with additives through hydrogen bonding interactions [1-5]. For example, addition of phosphoric acid derivatives such as hexamethylphosphoramide (HMPA) [1] and tri-*n*-butyl phosphate (TBP) [2] to radical polymerization of NIPAAm in toluene at low temperatures induced syndiotactic specificity. Polymer with 70% *racemo* (*r*) dyad content was obtained by

adding a 2-fold amount of HMPA relative to monomer in NIPAAm polymerization in toluene at –60°C. However, further decrease of the temperature to –80°C reduced the syndiotactic specificity.

Alkyl alcohols were also shown to induce syndiotactic specificity in NIPAAm polymerization in toluene at low temperatures [3]. The induced syndiotactic specificity depended on both the bulkiness of the added alcohol and the polymerization temperature. For instance, polymer with 71% *r* dyad content was obtained by polymerizing NIPAAm in toluene at –60°C in the presence of a 4-fold amount of 3-methyl-3-pentanol (3Me3PenOH), whereas 63% *r* dyad content was obtained by addition of methanol (MeOH) under the same conditions.

Poly(NIPAAm) has been extensively studied as a temperature-sensitive polymer material [6-8]. Recent developments in stereospecific polymerization have revealed that the stereoregularity of poly(NIPAAm) significantly affects the phase transition behavior [3, 5, 9-11]. Although our method is promising for facile preparation of syndiotactic poly(NIPAAm)s, further improvement of stereospecificity in NIPAAm polymerization is desired, because poly(NIPAAm) with higher syndiotacticity can be obtained by anionic polymerization of methoxymethyl-protected NIPAAm monomer [10].

Thus, radical polymerization of NIPAAm in the presence of both HMPA and alkyl alcohols was investigated, because further improvement in the syndiotactic specificity was expected by combining two kinds of syndiotactic specificity inducers. However, contrary to our expectations an increase in isotactic specificity was observed.

We report herein the results of polymerization of NIPAAm in the presence of both HMPA and alkyl alcohols, and propose a mechanism based on the structure of the hydrogen bonding-assisted complex formed byNIPAAm and the additives.

2. Experimental

2.1. Materials

NIPAAm (Tokyo Chemical Industry Co., Japan) was recrystallized from hexane-toluene mixture. Toluene was purified by washing with sulfuric acid, water and 5% aqueous NaOH, followed by fractional distillation. MeOH, ethanol (EtOH), acetonitrile, dichloromethane (Kanto Chemical Co., Japan), isopropyl alcohol (*i*PrOH), *tert*-butyl alcohol (*t*BuOH; Tokyo Chemical Industry Co., Japan), 3Me3PenOH, tri-*n*-butylborane (*n*-Bu_3B), purchased as a 1.0 M tetrahydrofuran (THF) solution, and HMPA (Aldrich Chemical Co., Japan) were used without further purification.

2.2. Polymerization

A typical polymerization procedure was as follows. NIPAAm (0.628 g, 5.5 mmol), HMPA (1.97 g, 11 mmol), and EtOH (0.506 g, 11 mmol) were diluted with toluene to a total volume of 5 ml, of which 4 ml was transferred to a glass ampoule and cooled to –80°C. Polymerization was initiated by adding an aliquot of *n*-Bu_3B solution (0.21 ml, 1.0 mol l^{-1}) to the solution. The reaction was terminated after 24 h by adding 2,6-di-*t*-butyl-4-methylphenol in THF (0.5 ml, 1.0 mol l^{-1}) at the polymerization temperature. The polymerization mixture was poured into diethyl ether (150 ml), and

the precipitated polymer was collected by filtration or centrifugation, and dried *in vacuo*. The polymer yield was determined gravimetrically.

2.3. Measurements

^{1}H and ^{13}C NMR spectra were obtained using an EX-400 spectrometer or an ECX-400 spectrometer (JEOL Ltd., Japan) operated at 400 MHz for ^{1}H and 100 MHz for ^{13}C. The dyad tacticity of the polymers was determined from the ^{1}H NMR signals of the methylene groups in the main chain, in deuterated dimethyl sulfoxide (DMSO-d_6) at 150°C. The triad tacticity of the polymers was determined from the ^{13}C NMR signals of the methine groups in the main chain, in a mixed solvent (DMSO-d_6:D_2O:$H(CF_2)_4CH_2OH$=75:10:15 wt%) at 100°C [5]. ^{1}H and ^{13}C NMR spectra of the mixture of NIPAAm, HMPA and/or EtOH were obtained in toluene-d_8 at –80°C. The molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography (SEC), using polystyrene samples as molecular weight standards. SEC was performed with an HLC 8220 chromatograph (Tosoh Co., Japan) equipped with TSK gel columns (SuperHM-M (6.5 mm ID×150 mm) and SuperHM-H (6.5 mm ID×150 mm), Tosoh Co., Japan). Dimethylformamide containing LiBr (10 mmol l^{-1}) was used as eluent at 40°C with flow rate 0.35 ml min^{-1}. The initial polymer concentration was 1.0 mg ml^{-1}.

3. Results and Discussion

3.1. Radical polymerization of NIPAAm in MeOH at low temperatures in the presence

or absence of HMPA

Radical polymerization of NIPAAm was carried out in MeOH at low temperatures for 24 h in the presence or absence of HMPA (Table 1). The *r* dyad contents of the polymers obtained in MeOH as solvent (Table 1, runs 1-5) were comparable with those obtained in toluene, although the *r* dyad content of the polymers obtained increased slightly with the use of MeOH as an additive in the NIPAAm polymerization in toluene [3]. It is suggested that decreasing the polarity of the polymerization system by dilution with toluene is important for the alcohol-mediated syndiotactic-specific radical polymerization of NIPAAm, because complex formation of NIPAAm monomer with alkyl alcohols, which is responsible for the induction of syndiotactic specificity, is efficiently promoted [12].

<Table 1>

The effect of HMPA on stereospecificity in NIPAAm polymerization in MeOH was examined (Table 1, runs 6-10). Regardless of the temperature, the *r* dyad contents of the polymers obtained were lower than those of the polymers prepared without HMPA. HMPA induced syndiotactic specificity in NIPAAm polymerization, even when polar molecules such as acetone and acetonitrile were used as solvents [12]. Thus, combining HMPA and alkyl alcohol brought about an unexpected effect on the stereospecificity of NIPAAm polymerization.

3.2. Effect of a combination of HMPA and alkyl alcohol on stereospecificity in the radical polymerization of NIPAAm

To examine the effect of a combination of HMPA and alkyl alcohol on the stereospecificity, polymerization of NIPAAm (1.0 mol l^{-1}) was carried out in toluene at low temperatures in the presence of both HMPA (2.0 mol l^{-1}) and MeOH (1.0 mol l^{-1}) (Table 2, runs 1-5). Fig. 1 shows the relationship between the polymerization temperature and the *r* dyad content of the polymers obtained. The *r* dyad contents of the polymers prepared in toluene in the presence or absence of HMPA [1] or MeOH [3] are also plotted in the Figure.

<Table 2>

<Fig. 1>

The *r* dyad contents of the polymers obtained at temperatures above –40°C increased slightly compared with those of the polymers obtained in the absence of the syndiotactic-specificity inducers, and were comparable with the *r* dyad contents of the polymers obtained in the presence of MeOH alone. However, further decrease of the temperature drastically decreased the *r* dyad content, and polymer rich in *m* dyad was obtained at –80°C. This means that the stereospecificity changed from syndiotactic to isotactic by reducing the polymerization temperature. A similar tendency was observed in the radical polymerization of NIPAAm in the presence of esters of phosphoric acid, such as TBP [2].

The effect of the structure of the added alcohol was investigated at –80°C in the presence of HMPA (Table 2, runs 5-8, 10, 14-20). Compared with the polymer obtained in the presence of HMPA alone (Table 2, run 8), addition of a less bulky alcohol such as MeOH or EtOH significantly increased the *m* dyad content of the polymers obtained (Table 2, runs 5-6, 10, and 14), whereas bulky alcohols such as *t*BuOH and 3Me3PenOH scarcely affected the stereoregularity (Table 2, runs 17-20). These results suggest that the combined effect is achieved only when less bulky alcohol was present together with HMPA at –80°C [13].

To examine the effect of the amounts of alkyl alcohol and HMPA on the stereospecificity, radical polymerization of NIPAAm (1.0 mol l^{-1}) was carried out in toluene at –80°C at several ratios of EtOH and HMPA (Table 2, runs 7-14). When the concentration of HMPA was kept at 2.0 mol l^{-1}, the *m* dyad content of the polymers obtained increased gradually with increase in $[EtOH]_0$ (Table 2, runs 8-10 and 14). Similarly, when the concentration of EtOH was kept at 2.0 mol l^{-1}, the *m* dyad content of the polymers obtained increased gradually with increase in $[HMPA]_0$ (Table 2, runs 11-14). In both cases, however, addition of alcohol or HMPA in excess was less effective, suggesting that equimolar amounts of both alcohol and HMPA relative to NIPAAm were necessary to significantly induce isotactic specificity.

3.3. Solvent effect of the isotactic specificity induced by a combination of HMPA and alkyl alcohol

Use of CH_3CN as solvent increased the isotactic specificity of radical

polymerization of NIPAAm at low temperatures [12]. To examine the solvent effect polymerization was carried out in CH_3CN at –40°C in the presence of both HMPA and less bulky alcohols such as MeOH and EtOH (Table 3, runs 1-6). The combined effect of HMPA and alkyl alcohol was observed, but the *m* dyad contents of the polymers were comparable with that of poly(NIPAAm) obtained in the absence of both HMPA and alkyl alcohol.

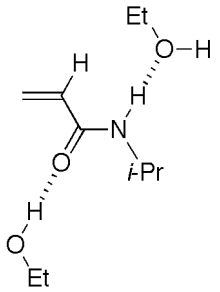
<Table 3>

CH_3CN was mixed with CH_2Cl_2 in 1:1 (vol:vol) proportion to carry out polymerization at –80°C [4]. Although the polymerizations proceeded heterogeneously, induced isotactic specificity was successfully enhanced [14], resulting in the formation of polymer with 67% *m* dyad content at relatively high yield.

3.4. Mechanistic considerations for the isotactic specificity induced by a combination of HMPA and alkyl alcohol

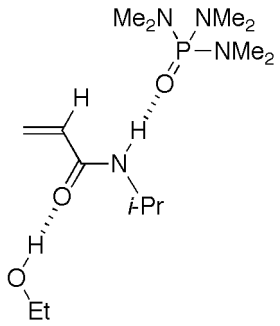
NMR analysis was carried out in toluene-d_8 at –80°C to examine the structure of the complex formed by NIPAAm and the additives (Fig. 2). On adding a 2-fold amount of EtOH to NIPAAm, the carbonyl carbon (C=O) and β-methylene carbon (H_2C=) signals exhibited downfield shifts, whereas the α-methine carbon (=CH) and amide proton (N-H) signals showed upfield shifts (Fig. 2a-b), suggesting that NIPAAm formed a 1:2 complex with ethanol through hydrogen bonding interaction as shown

below [3].



<Fig. 2>

Those signals, however, shifted in the reverse direction when HMPA in half the amount of NIPAAm was added to the NIPAAm-EtOH mixture (Fig. 2c). This tendency was enhanced with increase in the amount of HMPA (Fig. 2d-e). Addition of both HMPA and EtOH improved solubility of NIPAAm in toluene. As reported previously [1], HMPA formed 1:1 complex with NIPAAm through an N-H•••O=P hydrogen bonding, regardless of the temperature. Alcohol was suggested to form 1:2 complex with NIPAAm through a cooperative hydrogen bonding O-H•••O=C-N-H•••O [3]. In addition, fluorinated alcohol formed 1:1 complex with NIPAAm through an O-H•••O=C hydrogen bonding [5]. The NMR signals for a 1:2:2 mixture of NIPAAm:EtOH:HMPA (Fig. 2e) were sharper than those for NIPAAm alone (Fig. 2a), indicating that NIPAAm form hydrogen bonding interaction with HMPA and/or EtOH. The circumstantial evidence suggested that NIPAAm formed a 1:1:1 complex with EtOH and HMPA through cooperative hydrogen-bonding interactions [15-17] as shown below.



As reported previously [2], polymer rich in *m* dyad was obtained by radical polymerization of NIPAAm in toluene at –80°C in the presence of TBP, whereas polymer rich in *r* dyad was obtained under the same conditions except for increased temperature. The structure of the complex was assumed to be responsible for the change in stereospecificity, because NIPAAm formed a 1:1 complex at 0°C and a 1:2 complex at -80°C. In other words, larger steric hindrance by doubly coordinated TBPs changed the stereospecificity in NIPAAm polymerization (Scheme 1). A similar effect was observed in radical polymerization of methacrylates, where bulky monomers such as triphenylmethyl [18, 19] and 1-phenyldibenzosuberyl [20] methacrylates gave isotactic polymers, and less bulky monomers such as methyl methacrylate gave syndiotactic polymers.

<Scheme 1>

The cooperative hydrogen-bonding interaction in the 1:1:1 complex should strengthen each of the hydrogen-bonding interactions, i.e. O-H•••O=C and N-H•••O=P.

The strengthened N-H•••O=P hydrogen bond should enhance the steric hindrance of the coordinated HMPA compared with that in the 1:1 NIPAAm-HMPA complex. As a result of the enhanced steric hindrance of HMPA, isotactic specificity was significantly induced by a mechanism similar to that for polymerization of the methacrylates (Scheme 2).

<Scheme 2>

Table 4 summarizes the triad tacticities and the probabilities of *r*-addition to *m*-ended radical ($P_{m/r}$) and *m*-addition to *r*-ended radical ($P_{r/m}$) in first-order Markovian statistics for the polymers prepared in toluene at –80°C in the presence or absence of EtOH and/or HMPA. Stereoregulation obeyed Bernoullian statistics in the absence of syndiotactic specificity inducers, because the sum of the probabilities ($P_{m/r} + P_{r/m}$) was close to unity. Addition of HMPA not only influenced the stereospecificity of polymerization but also caused a deviation from the Bernoullian model, probably because the stereoselectivity of the propagating reaction in the HMPA-mediated syndiotactic-specific polymerization gradually varied with conversion [21].

<Table 4>

On the other hand, addition of EtOH obeyed the Bernoullian model, although the stereospecificity of polymerization was slightly affected. The addition of HMPA to

the polymerization system in the presence of EtOH also caused a deviation from the Bernoullian model, suggesting that the stereoselectivity of the propagating reaction varied with conversion even when HMPA was present together with EtOH. It should be noted that addition of HMPA drastically reduced the *r*-selectivity by *m*-ended radical, whereas the stereoselectivity by *r*-ended radical was only slightly affected. A similar tendency was observed in radical polymerization of methacrylates in toluene at 60°C; changing the monomer from diphenylmethyl methacrylate to triphenylmethyl methacrylate afforded syndiotactic and isotactic polymers, respectively [18, 22]. Consequently, the induced isotactic specificity was expected to arise predominantly from the increasing *m*-selectivity by *m*-ended radical due to the steric effect, enhanced by the cooperative hydrogen bonding interaction.

4. Conclusions

The combined effect of HMPA and alkyl alcohols on stereospecificity in NIPAAm polymerization was investigated. A combination of HMPA and less bulky alkyl alcohol induced isotactic specificity in the polymerization at –80°C, although both additives induced syndiotactic specificity when used separately. NMR analysis of the mixtures of NIPAAm and the additives suggested the formation of a 1:1:1 complex, assuming that isotactic specificity was induced by the steric effect of HMPA enhanced by a cooperative hydrogen bonding effect.

We concluded previously [21] that incorporation of monomer and/or the propagating chain-end free from complexation with HMPA was the reason that the

syndiotactic specificity induced by HMPA decreased by lowering the temperature to –80°C, because complex formation between NIPAAm and HMPA through N-H•••O=P hydrogen-bonding reduced the monomer reactivity due to the cross-conjugated structure of NIPAAm. The findings described in the present paper, however, suggest that the steric effect of HMPA enhanced by strengthened N-H•••O=P hydrogen-bonding interaction with decrease in the temperature to –80°C is an alternative reason for the reduction of the syndiotactic specificity induced by HMPA.

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13. Bulky alcohols such as 3Me3PenOH showed enhanced steric effect to improve syndiotactic specificity, when only alcohol was added into radical polymerization of NIPAAm in toluene at low temperatures [3]. In the polymerization system in this paper, however, combining alcohol and HMPA induced isotactic specificity, instead of syndiotactic specificity. Thus, it was suggested that dependence of bulkiness of the added alcohol on stereospecificity depended on the induced stereospecificity.

14. Addition of HMPA increased *m* dyad content of the polymer obtained in the mixed solvent (CH_3CN + CH_2Cl_2) at –80°C, probably because the solvent formed cooperative hydrogen bonding C-H•••O=C-N-H•••O=P with NIPAAm. In fact, HMPA-induced syndiotactic specificity of NIPAAm polymerization in CH_3CN or CH_2Cl_2 decreased even at –40°C or –60°C [12],

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22. Diphenylmethyl methacrylate: $P_{m/r}$=0.91 and $P_{r/m}$=0.27, triphenylmethyl methacrylate: $P_{m/r}$=0.15 and $P_{r/m}$=0.44. The values were calculated from the triad tacticities in the literature [18].

Table 1

Radical polymerization of NIPAAm in methanol for 24 h at low temperatures in the absence or presence of HMPA.

Run	$[HMPA]_0$	Temp.	Yield	Tacticity(%)[a]		M_n[b]	M_w/M_n[b]
	mol l^{-1}	°C	%	*m*	*r*	$\times 10^{-4}$	
1	0.0	0	67	45	55	3.31	1.9
2	0.0	–20	56	43	57	4.17	1.7
3	0.0	–40	54	43	57	5.02	1.7
4	0.0	–60	76	44	56	6.34	1.4
5	0.0	–80	75	46	54	7.64	1.7
6	2.0	0	32	46	54	2.30	1.4
7	2.0	–20	58	45	55	2.68	1.4
8	2.0	–40	78	50	50	3.31	1.5
9	2.0	–60	96	49	51	3.97	1.9
10[c]	2.0	–80	85	52	48	7.43	1.8

$[NIPAAm]_0$=1.0 mol l^{-1}, $[n\text{-}Bu_3B]_0$=0.10 mol l^{-1}.

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

b. Determined by SEC (polystyrene standards).

c. Monomer, polymer or both precipitated during the polymerization reaction.

Table 2

Radical polymerization of NIPAAm in toluene at low temperatures for 24 h in the presence of HMPA and alcohol.

Run	Added alcohol	$[Alcohol]_0$ mol l^{-1}	$[HMPA]_0$ mol l^{-1}	Temp. °C	Yield %	Tacticity(%)[a] *m*	*r*	M_n[b]× 10^{-4}	M_w/M_n[b]
1	MeOH	1.0	2.0	0	74	40	60	2.13	1.6
2	MeOH	1.0	2.0	–20	72	39	61	2.27	1.5
3	MeOH	1.0	2.0	–40	>99	39	61	2.26	2.5
4	MeOH	1.0	2.0	–60	98	42	58	1.86	2.2
5	MeOH	1.0	2.0	–80	64	53	47	0.87	1.7
6	MeOH	2.0	2.0	–80	76	55	45	1.69	1.5
7[c]	None	0.0	0.0	–80	78	46	54	3.85	2.7
8	None	0.0	2.0	–80	51	40	60	1.20	1.9
9	EtOH	0.5	2.0	–80	74	48	52	1.48	1.5
10	EtOH	1.0	2.0	–80	62	53	47	0.84	1.6
11	EtOH	2.0	0.0	–80	94	37	63	4.47	2.0
12	EtOH	2.0	0.5	–80	98	45	55	5.53	3.0
13	EtOH	2.0	1.0	–80	95	50	50	4.50	2.5
14	EtOH	2.0	2.0	–80	48	54	46	1.05	1.5
15	*i*PrOH	1.0	2.0	–80	45	47	53	2.12	1.7
16[c]	*i*PrOH	2.0	2.0	–80	60	48	52	2.57	2.0
17	*t*BuOH	1.0	2.0	–80	39	40	60	1.13	1.4
18[c]	*t*BuOH	2.0	2.0	–80	82	41	59	4.01	2.4
19[c]	3Me3PenOH	1.0	2.0	–80	39	43	57	1.20	1.4
20[c]	3Me3PenOH	2.0	2.0	–80	54	42	58	2.04	2.4

$[NIPAAm]_0$=1.0 mol l^{-1}, $[n\text{-}Bu_3B]_0$=0.10 mol l^{-1}, $[HMPA]_0$=2.0 mol l^{-1}.

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

b. Determined by SEC (polystyrene standards).

c. Monomer, polymer or both precipitated during the polymerization reaction.

Table 3

Radical polymerization of NIPAAm at low temperatures for 24 h in the presence of HMPA and alcohol.

Run	Solvent	Added alcohol	$[Alcohol]_0$ mol l^{-1}	$[HMPA]_0$ mol l^{-1}	Temp. °C	Yield %	Tacticity(%)[a] *m*	*r*	M_n[b]× 10^{-4}	M_w/M_n[b]
1	CH_3CN	None	0.0	0.0	–40	>99	57	43	2.09	1.6
2	CH_3CN	None	0.0	2.0	–40	89	50	50	0.80	1.6
3	CH_3CN	MeOH	2.0	0.0	–40	40	49	51	1.32	1.5
4	CH_3CN	MeOH	2.0	2.0	–40	88	58	42	1.11	1.9
5	CH_3CN	EtOH	2.0	0.0	–40	62	48	52	1.46	1.6
6	CH_3CN	EtOH	2.0	2.0	–40	89	55	45	1.30	1.7
7[c]	$CH_3CN+CH_2Cl_2$	None	0.0	0.0	–80	52	56	44	1.01	1.7
8[c]	$CH_3CN+CH_2Cl_2$	None	0.0	2.0	–80	85	60	40	2.64	1.5
9[c]	$CH_3CN+CH_2Cl_2$	MeOH	2.0	0.0	–80	64	47	53	2.08	2.1
10[c]	$CH_3CN+CH_2Cl_2$	MeOH	2.0	0.5	–80	61	52	48	3.49	2.5
11[c]	$CH_3CN+CH_2Cl_2$	MeOH	2.0	1.0	–80	94	61	39	2.26	1.8
12[c]	$CH_3CN+CH_2Cl_2$	MeOH	2.0	2.0	–80	64	67	33	4.11	1.3
13[c]	$CH_3CN+CH_2Cl_2$	EtOH	2.0	0.0	–80	91	42	58	4.01	2.1
14[c]	$CH_3CN+CH_2Cl_2$	EtOH	2.0	2.0	–80	>99	67	33	1.24	1.1

$[NIPAAm]_0$=1.0 mol l^{-1}, $[n\text{-}Bu_3B]_0$=0.10 mol l^{-1}.

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

b. Determined by SEC (polystyrene standards).

c. Monomer, polymer or both precipitated during the polymerization reaction.

Table 4

Triad tacticities and the probabilities of *r*-addition to *m*-ended radical ($P_{m/r}$), and *m*-addition to *r*-ended radical ($P_{r/m}$) in first-order Markovian statistics for the polymers prepared in toluene at –80°C in the presence or absence of EtOH and/or HMPA.

$[EtOH]_0$	$[HMPA]_0$	Triad tacticity(%)[a]			$P_{m/r}$	$P_{r/m}$	$P_{m/r}+P_{r/m}$
mol l^{-1}	mol l^{-1}	*mm*	*mr*	*rr*			
0.0	0.0	22	47	31	0.52	0.43	0.95
0.0	2.0	22	35	43	0.44	0.29	0.73
2.0	0.0	12	51	37	0.68	0.41	1.09
2.0	0.5	20	50	30	0.56	0.45	1.01
2.0	1.0	27	45	28	0.45	0.45	0.90
2.0	2.0	36	34	30	0.32	0.36	0.68

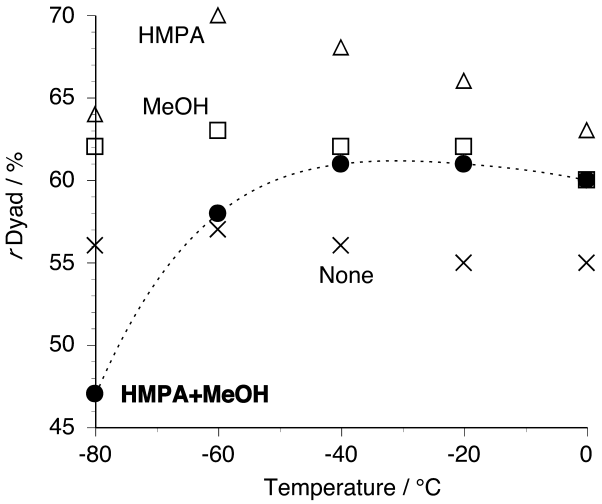


Fig. 1. Relationship between the polymerization temperature and *r* dyad content of poly(NIPAAm) prepared in toluene at low temperatures in the presence or absence of MeOH and/or HMPA.

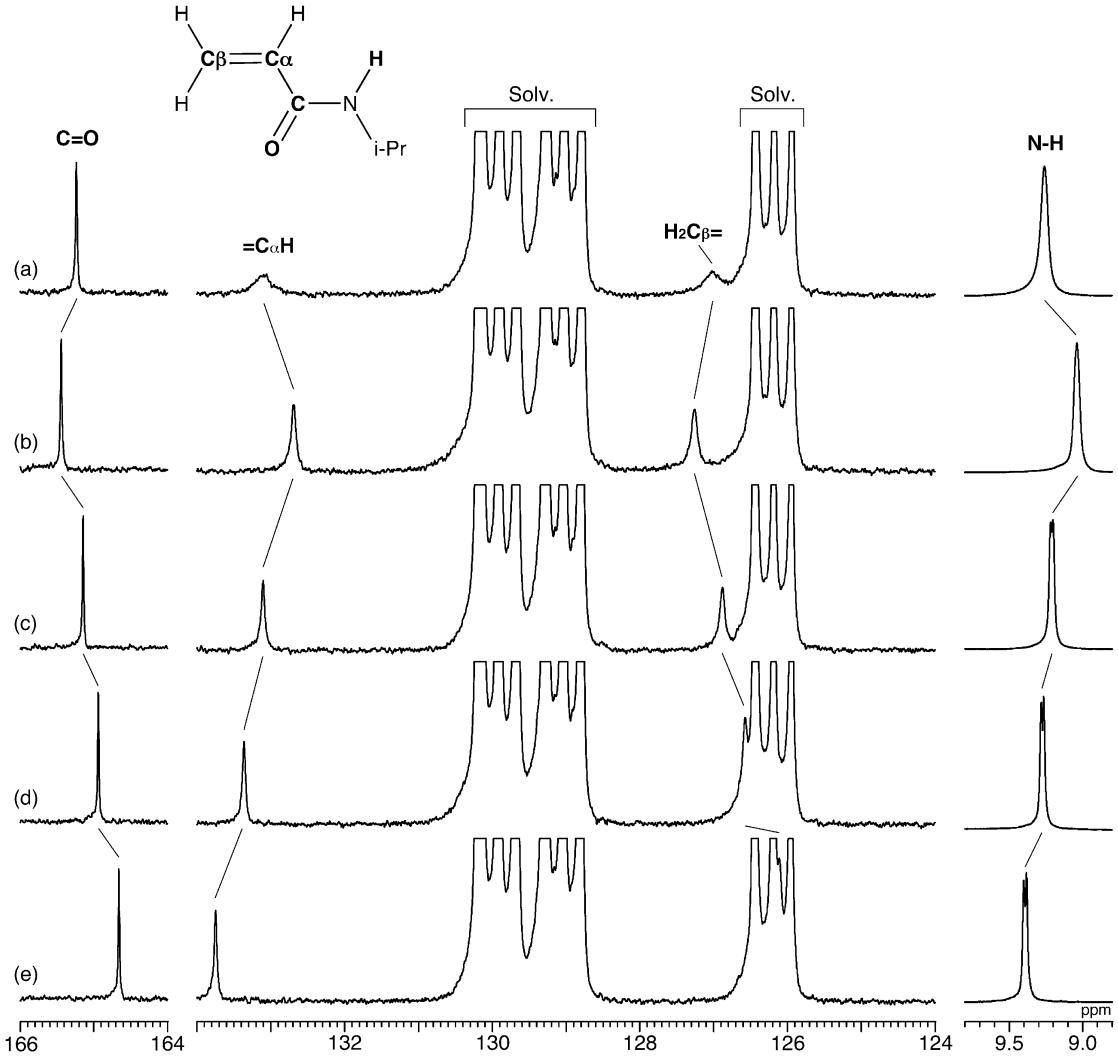
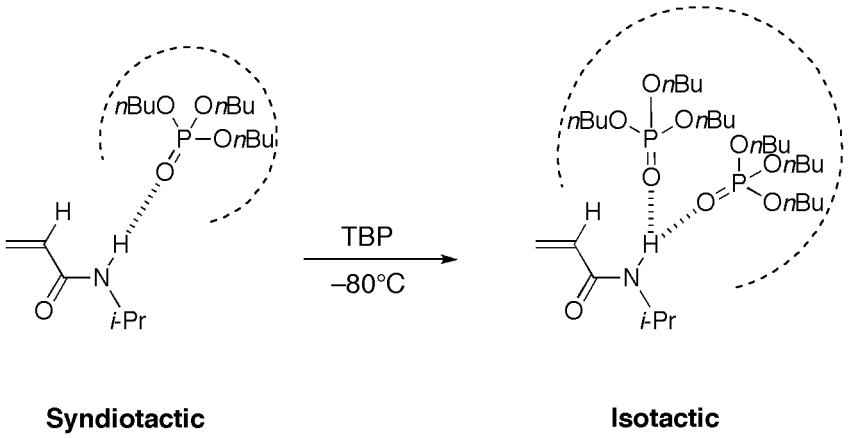
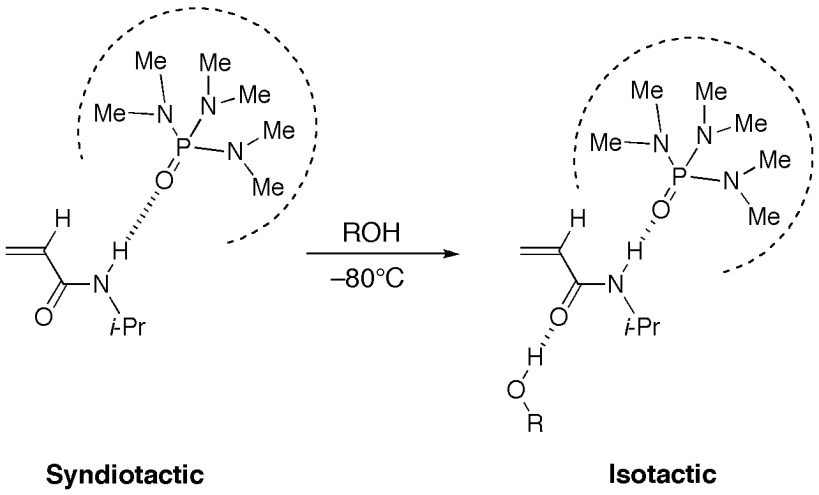


Fig. 2. Expanded ^{1}H and ^{13}C NMR spectra of NIPAAm ($[NIPAAm]_0$=0.2 mol l^{-1}) in toluene-d_8 at –80°C in the presence or absence of EtOH and/or HMPA. (a) $[EtOH]_0=[HMPA]_0$=0 mol l^{-1}; (b) $[EtOH]_0$=0.4 mol l^{-1}; (c) $[EtOH]_0$=0.4 mol l^{-1}, $[HMPA]_0$=0.1 mol l^{-1}; (d) $[EtOH]_0$=0.4 mol l^{-1}, $[HMPA]_0$=0.2 mol l^{-1}; (e) $[EtOH]_0$=0.4 mol l^{-1}, $[HMPA]_0$=0.4 mol l^{-1}.



Scheme 1. Change of the stereospecificity in NIPAAm polymerization from syndiotactic to isotactic because of the steric effect of TBP enhanced by formation of a 1:2 complex.



Scheme 2. Change of the stereospecificity in NIPAAm polymerization from syndiotactic to isotactic because of the steric effect of HMPA enhanced by formation of cooperative hydrogen bonding in the 1:1:1 complex.