

Isotactic-specific anionic polymerization of *N*-isopropylacrylamide with dilithium tetra-*tert*-butylzincate in the presence of a fluorinated alcohol or Lewis acid

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ABSTRACT

The polymerization of *N*-isopropylacrylamide (NIPAAm) with dilithium tetra-*tert*-butylzincate (TBZL) has been investigated in toluene at low temperatures in the presence of alkyl and fluorinated alcohols. Of the alcohols examined, 1,1,1,3,3,3-hexafluoro-2-propanol induced isotactic specificity and accelerated the polymerization process, affording the corresponding poly(NIPAAm)s in relatively high yields with *meso* (*m*) diad contents of 82%. It is worthy of note that the introduction of a fluorinated alcohol, which is typically used as an inhibitor in conventional anionic polymerization processes, enabled control over the stereospecificity and rate of the anionic polymerization of NIPAAm when TBZL was used as an initiator. Yttrium

trifluoromethanesulfonate also induced isotactic specificity in the NIPAAm polymerization process in methanol and gave poly(NIPAAm) in high yield with an *m* diad content of 88%.

Keywords: Anionic polymerization; *N*-Isopropylacrylamide; Isotactic

1. Introduction

N-Isopropylacrylamide (NIPAAm) does not undergo vinyl polymerization *via* a conventional anionic mechanism, because of the acidic proton of its amide group. Protection of the acidic proton is therefore required together with deprotection step following polymerization to provide poly(NIPAAm)s. In fact, there are reports in the literature describing the anionic polymerizations of protected NIPAAm monomers, followed by deprotection [1,2]. In these reports, stereocontrol of the anionic polymerization can be achieved, depending on the protecting group, initiator system and polymerization conditions, including the solvent and the temperature of the process. For instance, the polymerization of a trimethylsilyl-protected NIPAAm with a mixture of *tert*-BuLi and *n*-Bu₃Al in toluene at -40°C gave a highly isotactic poly(NIPAAm) with a *meso* (*m*) diad content of 97.3 % [1]. Furthermore, the polymerization of a methoxymethyl-protected NIPAAm with a mixture of 1,1-diphenyl-3-methylpentyllithium and diethylzinc in tetrahydrofuran (THF) at -78°C gave a syndiotactic poly(NIPAAm) with a *racemo* (*r*) diad content of 83%, whereas an isotactic polymer with an *m* diad content of 85 % was obtained when lithium chloride (LiCl) was used instead of diethylzinc [2].

Recently, dilithium tetra-*tert*-butylzincate (TBZL), which has been reported

as a bulky 'ate' complex, provided poly(NIPAAm)s directly *via* the anionic polymerization of unprotected NIPAAm monomers [3,4]. The direct anionic polymerization of unprotected NIPAAm monomers in these cases was attributed to the soft nucleophilicity and weak basicity of TBZL. Unfortunately, however, no information regarding the stereoregularities of the poly(NIPAAm) products formed according to these processes have been reported.

In contrast to direct anionic polymerization, a wide range of stereoregular poly(NIPAAm) materials are prepared by the radical polymerization of unprotected NIPAAm monomers. For instance, the addition of alkyl [5,6] and fluorinated alcohols [7,8] to NIPAAm polymerizations in toluene at low temperatures gave syndiotactic and heterotactic polymers, respectively. Furthermore, the introduction of a catalytic amount of a Lewis acid, such as yttrium trifluoromethanesulfonate [$Y(OTf)_3$], gave isotactic polymers in the polymerization of NIPAAm in methanol (MeOH) [9,10].

In the present paper, the anionic polymerization of NIPAAm with TBZL was investigated at low temperatures in the presence of alkyl alcohols, fluorinated alcohols, and $Y(OTf)_3$. These conditions effectively induced syndiotactic, heterotactic and isotactic specificity *via* radical mechanisms. It is therefore assumed that these additives significantly influence the stereosepecificity of the anionic polymerization of NIPAAm with TBZL. In fact, the induction of significant isotactic specificity was also successfully achieved in the anionic polymerization of unprotected NIPAAm monomers.

2. Experimental

2.1. Materials

NIPAAm (Tokyo Chemical Industry, Tokyo, Japan) was recrystallized from a hexane-toluene mixture prior to use. Toluene was purified by washing with sulfuric acid, water and 5% aqueous sodium hydroxide (NaOH) solution, followed by fractional distillation. MeOH (Kanto Chemical, Tokyo, Japan) was fractionally distilled. The TBZL solution in THF (supplied by Tosoh Finechem Corp., Yamaguchi, Japan), anhydrous ethanol (EtOH) (Wako Pure Chemical Industries, Osaka, Japan), 3-methyl-3-pentanol (3Me3PenOH), 2,2,2-trifluoroethanol (TFE), (Sigma-Aldrich Japan, Tokyo, Japan), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (supplied by Daikin Industries, Osaka, Japan), 2-propanol (*i*PrOH), nonafluoro-*tert*-butanol (NFTB), and Y(OTf)₃ (Tokyo Chemical Industry) were used as received.

The concentration of the *tert*-butyl group in the TBZL solution was determined to be 3.5 mol/L by hydrolysis with an excess of 0.1 N hydrogen chloride (HCl) solution and subsequent back-titration with a 0.1 N NaOH solution using phenolphthalein as an indicator. The concentrations of Zn²⁺ and Li⁺ were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (OPTIMA 3000, PerkinElmer Japan Co., Ltd., Yokohama, Japan) to be 0.84 and 3.0 mol/L, respectively. These values were consistent with a 1:2 molar mixture of *tert*-Bu₄ZnLi₂ and LiCl, with the latter being formed as a by-product of the reaction of *tert*-butyllithium and zinc chloride (ZnCl₂) during the preparation of TBZL. The concentration of TBZL was calculated as being one-fourth the concentration of the *tert*-butyl group, based on the assumption that only one of the four *tert*-butyl groups on Zn participates in the initiating reaction.

2.2. Polymerization

A typical polymerization procedure was as follows. NIPAAm (0.28 g, 2.5 mmol) and HFIP (1.68 g, 10.0 mmol) were dissolved in toluene to a total volume of 5.0 mL. A portion (4.0 mL) of the resulting solution was transferred to a glass ampoule and cooled to -60°C . The glass ampoule was degassed and filled with nitrogen six times. The polymerization was initiated by the addition of an aliquot of TBZL (2.0 mol% relative to the monomer; 0.047 mL, 0.86 mol/L) in THF to the solution. The reaction was subsequently terminated after 16 h by the addition of methanolic solution of 2 N HCl at the polymerization temperature. The resulting mixture was then poured into diethyl ether (400 mL) and the precipitated polymer was collected by centrifugation and dried *in vacuo*. The polymer yield was determined gravimetrically.

2.3. Measurements

^1H NMR spectra (400 MHz) were obtained using an EX-400 or ECX-400 spectrometer (JEOL Ltd., Tokyo, Japan). Deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) was used as a solvent for NMR analysis. The diad tacticity of the poly(NIPAAm)s was determined from the ^1H NMR signals of the methine and methylene groups in the main chain at 150°C .

3. Results and discussion

3.1. The polymerization of NIPAAm with TBZL in toluene and in MeOH

The polymerization of NIPAAm with TBZL was investigated in both toluene and MeOH at a variety of different temperatures over a 16 h period (Table 1). Polymer yields for the polymerizations in MeOH at higher temperatures tended to be higher than the corresponding yields when the process was conducted in toluene. These results were

consistent with reports from the literature [3] in which the use of protic solvents was found to accelerate the polymerization of NIPAAm. Polymers rich in *m* diad were obtained in toluene, regardless of temperature used (Table 1, runs 1-6). In contrast, the *m* diad content of the polymers formed in MeOH increased gradually with decreasing temperature, and provided almost atactic polymers (Table 1, runs 7-13). This result corresponded well with the solvent-dependency of the stereospecificity typically observed in the anionic polymerizations of (meth)acrylates, in which the isotactic specificity increases in non-polar solvents such as toluene [11,12].

Table 1

Polymerization of NIPAAm with TBZL in toluene and MeOH for 16 h period

Run	Solvent	Temp.	Yield	Diad / % ^a		$M_{n(\text{Obsd})}$ ^b	$M_{n(\text{Calcd})}$ ^c	f^d
		°C		%	m	r	10^3	
1	Toluene	40	22	59	41	6.7	1.3	0.19
2	Toluene	20	20	58	42	5.6	1.2	0.21
3	Toluene	0	23	56	44	7.0	1.3	0.19
4	Toluene	-20	11	59	41	3.4	0.7	0.20
5	Toluene	-40	13	60	40	4.0	0.8	0.20
6	Toluene	-60	9	57	43	3.5	0.6	0.16
7	MeOH	40	>99	47	53	16.0	5.7	0.36
8	MeOH	20	33	47	53	16.9	1.9	0.11
9	MeOH	0	83	46	54	24.8	4.8	0.19
10	MeOH	-20	85	45	55	22.7	4.9	0.22
11	MeOH	-40	23	48	52	5.4	1.4	0.25
12	MeOH	-60	16	50	50	4.0	1.0	0.25
13	MeOH	-80	10	51	49	3.9	0.6	0.15

[NIPAAm]₀ = 0.5 mol/L, [TBZL]₀ = 2.0 mol%.a. Determined from the ¹H NMR signals of the methine and methylene groups in the main chain.b. Determined from the ¹H NMR signals of the $\text{-NCH(CH}_3)_2$ and *tert*-butyl groups.c. Calculated with the following equation: $M_{n(\text{Calcd})} = 113.16 (MW_{\text{NIPAAm}}) \times 50 ([\text{NIPAAm}]_0 / [\text{TBZL}]_0) \times \text{yield} / 100 + 58.12 (MW_{\text{tert-Bu-H}})$

d. Initiator efficiency.

The molecular weights of the poly(NIPAAm)s were difficult to determine by size-exclusion chromatography because the polymers were adsorbed on the stationary phase. In particular, no elution peaks were detected for the poly(NIPAAm)s with high *m* diad contents even under the same conditions as reported previously [5-8]. The chain-end structures of the poly(NIPAAm)s prepared with TBZL were reported to be composed of *tert*-butyl group at the initiating chain-end and hydrogen at the terminating chain-end [3]. The ¹H NMR spectrum of poly(NIPAAm) prepared with TBZL in MeOH

at -60°C (Table 1, run 12) is shown in Fig. 1. As expected, a resonance corresponding to the *tert*-butyl group derived from TBZL was clearly present in the spectrum. The molecular weights of the polymers were subsequently estimated by end-group analysis of the *tert*-butyl proton signals and the signals of the methine protons in the isopropyl groups, based on the assumption that the polymerization was initiated only from the *tert*-butyl groups on TBZL. A similar technique has been adopted for estimating the molecular weights of isotactic poly(NIPAAm)s derived from anionic polymerization of a trimethylsilyl-protected NIPAAm with a mixture of *tert*- $\text{C}_4\text{H}_9\text{Li}$ and *n*- $(\text{C}_4\text{H}_9)_3\text{Al}$ [1].

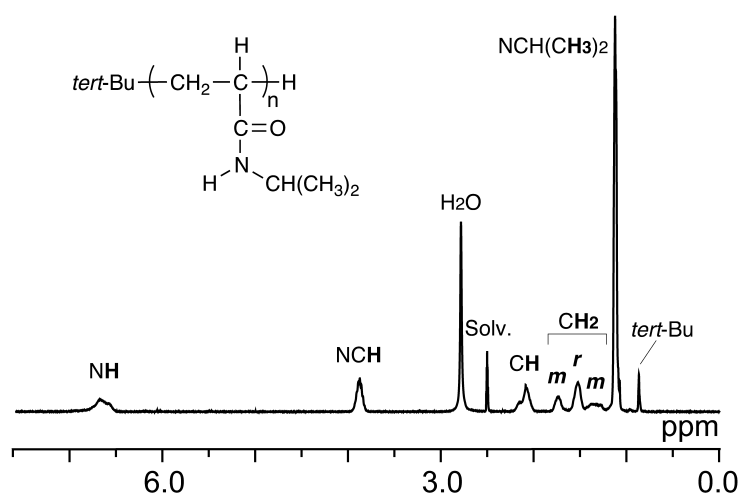


Fig. 1. ^1H NMR spectrum of poly(NIPAAm) prepared with TBZL in MeOH at -60°C (Table 1, run 12).

The molecular weights of the poly(NIPAAm)s obtained in MeOH at higher temperatures tended to be higher than the corresponding polymers obtained in toluene. The effect of the solvent on the molecular weights of the polymers became less pronounced with decreasing temperature. These corresponded well with the results

observed for polymer yields mentioned above. The initiator efficiency (f) value was found to be much less than unity and was independent of the solvent and temperature used, which corresponded well with results previously published in the literature [3,4].

3.2. Polymerization of NIPAAm with TBZL in toluene in the presence of alcohols

The polymerization of NIPAAm with TBZL was investigated in toluene at low temperatures over a 16 h period in the presence of alkyl alcohols, which were introduced in a four-fold excess relative to the monomer (Table 2). The alkyl alcohols were added because they have been reported to induce syndiotactic specificity and to also accelerate polymerization in the radical polymerization of NIPAAm in toluene [5,6]. The addition of less bulky alcohols, such as MeOH and EtOH, significantly increased both polymer yields and molecular weights relative to the corresponding reactions conducted in the absence of alkyl alcohols (see Table 1). The m diad contents of the polymers, however, ranged between the values obtained in toluene and the values obtained in MeOH. In contrast, the addition of bulkier alcohols, such as *i*PrOH and 3Me3PenOH, had little impact on the polymerization behavior. These results suggested that the alkyl alcohols did not exert any positive influence over the control of the stereospecificity in the polymerization of NIPAAm with TBZL.

Table 2

Polymerization of NIPAAm with TBZL in toluene for 16 h in the presence of alkyl alcohols

Run	Added alcohol	Temp.	Yield	Diad / % ^a		$M_{n(\text{Obsd})}^b$	$M_{n(\text{Calcd})}^c$	f^d
		°C		%	m	r	10^3	
1	MeOH	0	63	48	52	26.3	3.6	0.14
2	MeOH	-20	54	48	52	13.3	3.1	0.23
3	MeOH	-40	30	54	46	6.4	1.7	0.27
4	MeOH	-60	17	55	45	4.6	1.0	0.23
5	EtOH	0	37	50	50	15.8	2.1	0.14
6	EtOH	-20	27	52	48	12.4	1.6	0.13
7	EtOH	-40	10	59	41	3.6	0.6	0.17
8	EtOH	-60	12	56	44	2.0	0.7	0.37
9	iPrOH	0	9	59	41	2.2	0.6	0.26
10	iPrOH	-20	11	60	40	4.5	0.7	0.15
11	iPrOH	-40	10	60	40	3.4	0.6	0.19
12	iPrOH	-60	11	58	42	4.7	0.7	0.15
13	3Me3PenOH	0	16	58	42	4.4	1.0	0.22
14	3Me3PenOH	-20	14	62	38	1.7	0.8	0.50
15	3Me3PenOH	-40	15	61	39	1.8	0.9	0.51
16	3Me3PenOH	-60	8	60	40	2.6	0.5	0.20

[NIPAAm]₀ = 0.5 mol/L, [TBZL]₀ = 2.0 mol%, [Alcohol]₀ = 2.0 mol/L.

a. Determined from the ¹H NMR signals of the methine and methylene groups in the main chain.

b. Determined from the ¹H NMR signals of the $\text{-NCH(CH}_3)_2$ and *tert*-butyl groups.

c. Calculated with the following equation: $M_{n(\text{Calcd})} = 113.16 (\text{MW}_{\text{NIPAAm}}) \times 50 ([\text{NIPAAm}]_0 / [\text{TBZL}]_0) \times \text{yield} / 100 + 58.12 (\text{MW}_{\text{tert-Bu-H}})$

d. Initiator efficiency.

We proceeded to investigate the NIPAAm polymerizations with TBZL in the presence of a four-fold excess of several fluorinated alcohols (Table 3) because the induction of heterotactic specificity had been reported in the radical polymerization of NIPAAm under the corresponding conditions [7,8]. The addition of TFE led to significant increases in both the polymer yields and the f values, whereas only moderate

increases in the m diad contents of the polymers were observed (Table 3, runs 1-4). Furthermore, the yields and molecular weights of the polymers tended to increase with decreasing polymerization temperature. These results suggested that TFE affected the polymerization behavior through a hydrogen bonding interaction. Even in the presence of the more acidic NFTB ($pK_a = 5.2$) [13], polymers were still obtained (Table 3, runs 19-21). Unfortunately, however, the addition of NFTB at 0 and -20°C had little impact on the polymerization behavior, whereas the addition at -40°C significantly increased the f value and provided an almost atactic polymer. Of the added fluorinated alcohols, HFIP significantly increased the yields, f values, and m diad contents of the polymers (Table 3, runs 5-7 and 17) and these values were further enhanced with decreasing temperature. In particular, poly(NIPAAm)s with m diad contents of 82% were obtained at lower temperatures (Fig. 2b).

Table 3

Polymerization of NIPAAm with TBZL in toluene in the presence of fluorinated alcohols (RfOHs)

Run	Added alcohol	[RfOH] ₀	Temp.	Time	Yield	Diad / % ^a		$M_{n(\text{Obsd})}^b$	$M_{n(\text{Calcd})}^c$	f^d
		mol l ⁻¹	°C	h	%	<i>m</i>	<i>r</i>	10 ³	10 ³	
1	TFE	2.0	0	16	35	62	38	2.7	2.0	0.75
2	TFE	2.0	-20	16	47	58	42	7.6	2.7	0.36
3	TFE	2.0	-40	16	>99	59	41	10.0	5.7	0.57
4	TFE	2.0	-60	16	86	61	39	9.8	4.9	0.50
5	HFIP	2.0	0	16	9	68	32	3.7	0.6	0.15
6	HFIP	2.0	-20	16	12	75	25	5.1	0.7	0.14
7	HFIP	2.0	-40	16	23	82	18	7.6	1.3	0.18
8	HFIP	0.25	-60	16	47	62	38	7.3	2.7	0.38
9	HFIP	0.5	-60	16	60	67	33	8.1	3.5	0.43
10	HFIP	1.0	-60	16	77	77	23	11.9	4.4	0.37
11	HFIP	1.5	-60	16	58	81	19	12.6	3.3	0.26
12	HFIP	2.0	-60	0.5	23	82	18	3.2	1.4	0.43
13	HFIP	2.0	-60	1	33	81	19	8.5	1.9	0.23
14	HFIP	2.0	-60	2	52	82	18	9.8	3.0	0.31
15	HFIP	2.0	-60	4	72	81	19	14.5	4.1	0.28
16	HFIP	2.0	-60	8	80	82	18	16.3	4.6	0.28
17	HFIP	2.0	-60	16	73	82	18	14.9	4.2	0.28
18	HFIP	2.0	-60	24	93	81	19	15.8	5.3	0.34
19	NFTB	2.0	0	16	12	60	40	3.2	0.7	0.23
20	NFTB	2.0	-20	16	12	59	41	3.8	0.8	0.20
21	NFTB	2.0	-40	16	25	52	48	1.9	1.5	0.75

[NIPAAm]₀ = 0.5 mol/L, [TBZL]₀ = 2.0 mol%.

a. Determined from the ¹H NMR signals of the methine and methylene groups in the main chain.

b. Determined from the ¹H NMR signals of the $\text{-NCH}(\text{CH}_3)_2$ and *tert*-butyl groups.

c. Calculated with the following equation: $M_{n(\text{Calcd})} = 113.16 (\text{MW}_{\text{NIPAAm}}) \times 50 ([\text{NIPAAm}]_0/[\text{TBZL}]_0) \times \text{yield}/100 + 58.12 (\text{MW}_{\text{tert-Bu-H}})$

d. Initiator efficiency.

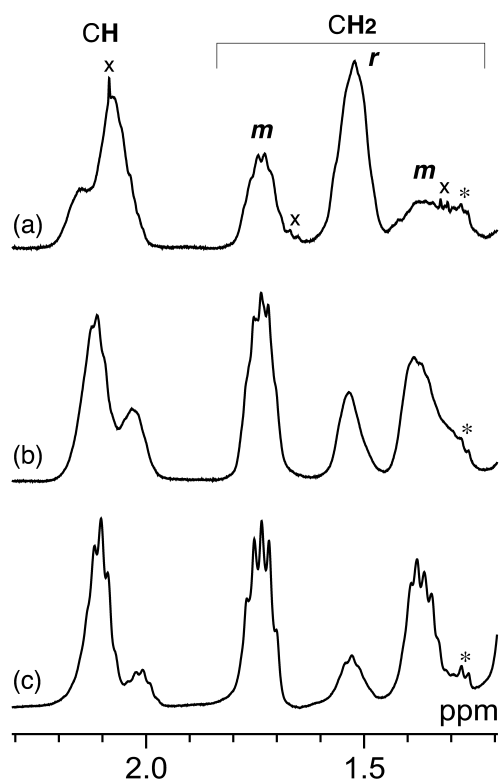


Fig. 2. ^1H NMR spectra of the methine and methylene groups in the main-chain of poly(NIPAAm)s prepared (a) in MeOH at -60°C (Table 1, run 12), (b) in toluene at -60°C in the presence of HFIP (Table 3, run 17), and (c) in MeOH at -20°C in the presence of $\text{Y}(\text{OTf})_3$ (Table 4, run 2). The asterisk indicates the ^{13}C satellite peak from the $(\text{CH}_3)_2\text{CH}-$ groups. The x denotes impurities.

The polymerization of NIPAAm in the presence of HFIP at -60°C was investigated in greater detail (Table 3, runs 8-11 and 17). The yield and *m* diad content of the polymer was found to gradually increase as the amount of HFIP added was increased. This suggested that an excess of HFIP was required to induce a significant level of isotactic specificity. The effect of polymerization time was then examined in the presence of an excess amount of HFIP (Table 3, runs 12-18). The yield and the molecular weight of the poly(NIPAAm) was found to gradually increase with increasing

polymerization time, implying the living character of the current polymerization system. Unfortunately, however, the f values were much lower than unity and did not reach a fixed value. Consequently, the polymer yield varied, even when the polymerizations were carried out repeatedly under the same conditions. Thus, a more detailed investigation using freshly prepared TBZL is still required to confirm the living nature of the current system.

3.3. NMR analysis in the vicinity of the initiating chain-end

End-group analysis of the polymers by NMR spectroscopy often provides important information for developing an understanding of the polymerization mechanism [14,15]. The expanded ^1H NMR spectra of the *tert*-butyl groups of the poly(NIPAAm)s prepared in toluene at -60°C using different amounts of HFIP (cf. Table 3, runs 8-11 and 17) are shown in Fig. 3. The ^1H NMR signals of the *tert*-butyl groups derived from TBZL exhibited splitting, likely because of longer than triad or tetrad stereosequences near the initiating chain-end. Although the living nature of the current polymerization process remains uncertain, the splitting of the *tert*-butyl group resonances reflects the stereoselectivity of the initiating species.

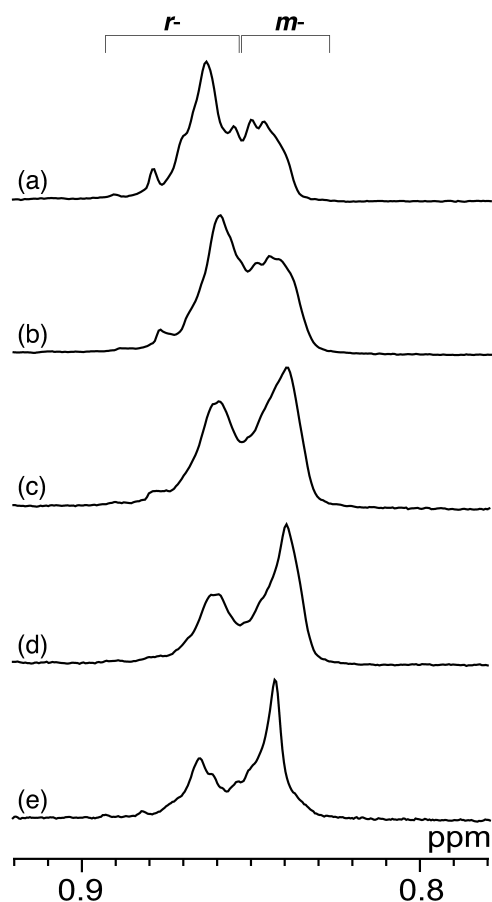
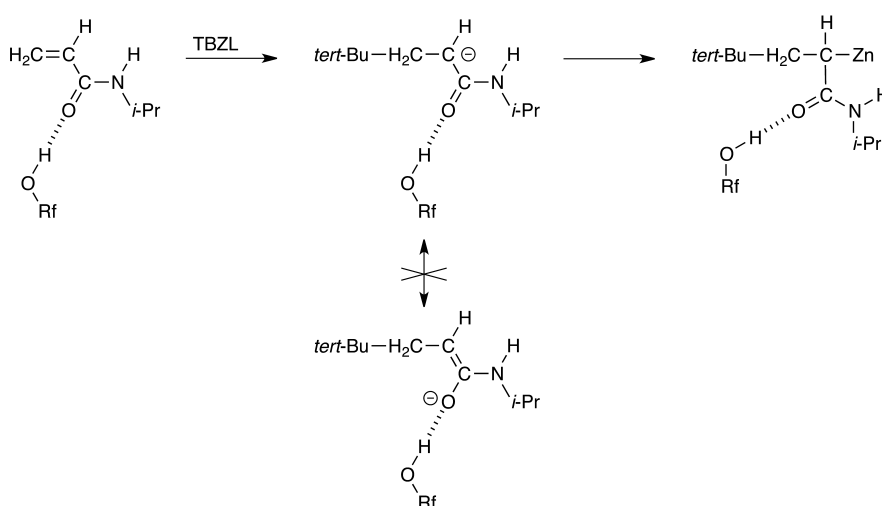


Fig. 3. ^1H NMR spectra of the *tert*-butyl groups of the poly(NIPAAm)s prepared with TBZL in toluene at -60°C in the presence of different amounts of HFIP. $[\text{HFIP}]_0/[\text{NIPAAm}]_0 =$ (a) 0.5, (b) 1.0, (c) 2.0, (d) 3.0, and (e) 4.0.

The *tert*-butyl group resonances were effectively split into two peaks, potentially as a consequence of the diad stereosequences near the initiating chain-end. The relative intensities of the peaks at the higher magnetic fields increased with increasing $[\text{HFIP}]_0/[\text{NIPAAm}]_0$ ratio. Considering that the *m* diad content in the main chain gradually increased with increasing HFIP, the peaks can be assigned at diad levels, as shown in Fig. 3. Furthermore, the signals of the *tert*-butyl groups sharpened as the $[\text{HFIP}]_0/[\text{NIPAAm}]_0$ ratio increased. It was assumed that the initiating species, such as

dimer and trimer anions, had a preference for *m*-addition over *r*-addition in the presence of an excess amount of HFIP.

We previously reported that NIPAAm monomers and fluorinated alcohols form 1:1 complex through a C=O...H-O hydrogen bonding interaction (Scheme 1) [8]. The attack of the TBZL *tert*-butyl group on the β carbon of the complexed NIPAAm monomer in the initiation reaction leads to the formation of the corresponding carbanion. The resulting carbanion can then be transformed into enolate anion, which is believed to be the key reactive species in the typical anionic polymerizations of α,β -unsaturated carbonyl monomers. In the current system, however, the fluorinated alcohol binding to the carbonyl group through a hydrogen bonding interaction would quench the activity of the enolate anion as soon as it was formed. It was therefore assumed that the key active species in the current system was the carbanion, which would be stabilized through a C-Zn bond. Similar structures have been reported for typical Reformatsky reagents [16-19].



Scheme 1. Proposed structure of the propagating species stabilized by a C-Zn bond in the current system.

Although the mechanism for the induction of isotactic specificity remains unclear, it has been assumed that the carbanion is the active species in the process and is responsible for the observed difference in stereospecificities, induced by HFIP, between the radical and anionic polymerization processes of NIPAAm.

3.4. Polymerization of NIPAAm with TBZL in MeOH in the presence of Y(OTf)₃

The introduction of a catalytic amount of a Lewis acid such as Y(OTf)₃ has been reported to induce isotactic specificity in the radical polymerization of NIPAAm in MeOH [9,10]. With this in mind, we proceeded to investigate the effect of Y(OTf)₃ on the NIPAAm polymerization in the presence of TBZL (Table 4). With the exception of the polymerization performed at -60°C, the addition of Y(OTf)₃ led to significant increases in the yields and *m* diad contents of the resulting polymers, whereas the *f* values remained relatively unchanged. In particular, poly(NIPAAm) with an *m* diad content of 88% was obtained at -20°C (Fig. 2c). These results indicated that Y(OTf)₃ played an important role in the isotactic specificity of the anionic polymerization of NIPAAm as well as in the radical polymerization of NIPAAm.

Table 4

Polymerization of NIPAAm with TBZL in MeOH for 16 h in the presence of Y(OTf)₃

Run	Temp.	Yield	Diad / % ^a		$M_{n(\text{Obsd})}^b$	$M_{n(\text{Calcd})}^c$	f^d
	°C		m	r	10^3	10^3	
1	0	>99	86	14	45.1	5.7	0.13
2	-20	>99	88	12	26.7	5.7	0.21
3	-40	98	87	13	23.2	5.6	0.24
4	-60	69	81	19	14.3	4.0	0.28

[NIPAAm]₀ = 0.5 mol/L, [TBZL]₀ = 2.0 mol%, [Y(OTf)₃]₀ = 0.05 mol/L.

a. Determined from the ¹H NMR signals of the methine and methylene groups in the main chain.

b. Determined from the ¹H NMR signals of $\text{-NCH}(\text{CH}_3)_2$ and *tert*-butyl groups.

c. Calculated with the following equation: $M_{n(\text{Calcd})} = 113.16 (\text{MW}_{\text{NIPAAm}}) \times 50 ([\text{NIPAAm}]_0 / [\text{TBZL}]_0) \times \text{yield} / 100 + 58.12 (\text{MW}_{\text{tert-Bu-H}})$

d. Initiator efficiency.

4. Conclusions

The polymerization of NIPAAm with TBZL was investigated in toluene and in MeOH in the presence of alkyl alcohols, fluorinated alcohols, or Y(OTf)₃. HFIP and Y(OTf)₃ were found to induce isotactic specificity and accelerate the polymerization process.

An understanding of how HFIP efficiently induced the isotactic specificity and accelerated the polymerization process remains unclear at present. It is worthy of note, however, that the stereospecificity and rate of the anionic polymerization of NIPAAm, which has an acidic proton, could be controlled by the addition of a fluorinated alcohol when TBZL was used as an initiator, even though the fluorinated alcohol usually behaves as an inhibitor in conventional anionic polymerization

processes. We believe that the key active species in the polymerization process is the carbanion stabilized by a C-Zn bond, which is responsible for the unusual polymerization behaviors.

These results suggest that the combination of TBZL with a fluorinated alcohol would present significant potential for the development of novel research opportunities, such as a stereospecific anionic polymerization controlled by a hydrogen-bonding interaction. Further work is now under way to reveal the mechanism of the induced isotactic specificity and to confirm the living nature of the current system.

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