Dual Roles of Alkyl Alcohols as Syndiotactic-Specificity-Inducer and Accelerator in the Radical Polymerization of *N*-Isopropylacrylamide and Some Properties of Syndiotactic Poly(*N*-isopropylacrylamide)

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Abstract: Effect of simple alkyl alcohol on radical polymerization of *N*-isopropylacrylamide (NIPAAm) in toluene at low temperatures was investigated. We succeeded in induction of syndiotactic-specificity and acceleration of polymerization reaction at the same time by adding simple alkyl alcohols such as 3-methyl-3-pentanol (3Me3PenOH) into NIPAAm polymerization. The diad syndiotacticity increased with a decrease in temperature and an increase in bulkiness of the added alcohol, and reached up to 71% at –60°C in the presence of 3Me3PenOH. With the aide of NMR analysis, it was revealed that alcohol compounds play dual roles in this polymerization system; alcohol compound coordinating to N-H proton induces the syndiotactic-specificity and

that hydrogen-bonded to C=O oxygen accelerates the polymerization reaction. The effect of syndiotacticity on properties of poly(NIPAAm)s was also discussed in some detail.

Keywords: hydrogen bond; *N*-isopropylacrylamide; alcohol; syndiotactic-specific radical polymerization; lower critical solution temperature

INTRODUCTION

Porter *et al* have reported preparation of highly isotactic polymers by radical polymerization of acrylamide derivatives, in which chiral groups, such as chiral oxazolidine, were employed as stereocontrolling auxiliaries.[1,2] Okamoto *et al*. have reported condition-controlled isotactic-specific radical polymerization of acrylamide derivatives, in which catalytic amounts of Lewis acids, such as yttrium trifluoromethanesulfonate, were employed as stereocontrolling auxiliaries.[3-6] The both polymerization systems provided isotactic polymers with *meso* (*m*) diad content over 90%.[1-7] Thus, the isotactic-specificity in radical polymerization of acrylamide derivatives has been successfully achieved until it is comparable to anionic or coordination polymerizations.[8-14]

On the other hand, preparation of highly syndiotactic polymers by radical polymerization of acrylamide derivatives had been hardly reported, except for the following systems; (1) a syndiotactic polymer with *racemo* (*r*) diad content of 93% (*N,N*-diphenylacrylamide in tetrahydrofuran at –98°C),[15] (2) a syndiotactic polymer with *r* diad content of 76% (3-acryloyl-2-oxazolidinone in toluene at –78°C).[16] The syndiotacticity

of the former is comparable to those of polymers obtained via anionic polymerizations of

N,N-disubstituted acrylamides.[11,13] The stereochemistry, however, strongly depends on

the structure of the monomers; N,N-dimethylacrylamide provided isotactic polymers

under the corresponding polymerization conditions.[15] Thus, the development of

condition-controlled syndiotactic-specific radical polymerization of acrylamide

derivatives has been strongly desired.

Recently, we have found that a hydrogen-bonding interaction between N-isopropylacrylamide (NIPAAm) and Lewis base is available for controlling

stereospecificity of radical polymerization of NIPAAm.[17-20] The hydrogen-bond-induced

stereospecificity depended on polymerization conditions such as the kind of the added

Lewis base and the solvent. Isotactic poly(NIPAAm) with m diad content of 61% was

obtained at –60°C in chloroform in the presence of pyridine N-oxide.[19] Syndiotactic

poly(NIPAAm)s were obtained in toluene in the presence of phosphoric acid

derivatives.[17,18,20] In particular, by adding an excess amount of

hexamethylphosphoramide (HMPA), the diad syndiotacticity of the obtained

poly(NIPAAm)s reached up to 72% that is the highest syndiotacticity among those of the

radically prepared poly(NIPAAm)s.[17c] Thus, we made the first step to fulfill the above-

mentioned desire. However, this polymerization requires careful operation, because of

the toxicity of HMPA. So, as the next target, we focused our interest on the development

of syndiotactic-specific polymerization induced by safer reagents instead of HMPA.

It is known that alcohol compounds play efficient roles in controlling

stereospecificity of radical polymerization of vinyl monomers.[21-27] In particular,

fluoroalcohol compounds, such as 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and perfuloro-*t*-butanol, exhibit significant stereoregulating power in radical polymerization of ester monomers such as vinyl esters[22] and methacrylates.[23,25] Recently, we also found that not only HFIP but also simple alkyl alcohols such as *t*-butanol (*t*-BuOH) significantly decreased syndiotactic-specificity in radical polymerization of *N*-vinylacetamide (NVA),[27] although simple alkyl alcohols hardly affected the stereospecificity in the polymerization of vinyl esters[22] and methacrylates.[23] This is probably because Lewis basicity of carbonyl group of amide group in NVA is stronger than those of ester monomers. Thus, we started investigating the effect of simple alkyl alcohols on the stereospecificity in radical polymerization of NIPAAm, which is also one of monomers containing amide group as well as NVA. Here, we report a successful induction of syndiotactic-specificity and acceleration in NIPAAm polymerization by adding simple alkyl alcohols. The effect of the syndiotacticity on the thermal and solution properties of poly(NIPAAm)s is also discussed in some detail.

EXPERIMENTAL

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. Methanol (MeOH) and ethanol (EtOH) were distilled before the use. Tri-*n*-butylborane (*n*-Bu$_3$B) as a tetrahydrofuran (THF) solution (1.0M), HMPA (Aldrich Chemical Co.), *t*-BuOH (Wako.

Co), isopropanol (*i*-PrOH) and 3-methyl-3-pentanol (3Me3PenOH) (Tokyo Kasei Kogyo

Co.) were used without further purification for polymerization reaction.

Polymerization

Typical polymerization procedure is as follows; NIPAAm (0.314 g, 2.8 mmol)

was dissolved in toluene to prepare a 5 mL solution (0.56 mol/L). Four milliliter of the

solution was transferred to the glass ampoule and cooled at 0°C. The polymerization was

initiated by adding *n*-Bu$_3$B solution (0.22 mL) into the monomer solution. After 24h, the

reaction was terminated with a small amount of THF solution of 2,6-di-*t*-butyl-4-

methylphenol at polymerization temperature. The polymerization mixture was poured

into a large amount of diethyl ether, and the precipitated polymer was collected by

filtration or centrifugation, and dried *in vacuo*. The polymer yield was determined

gravimetrically.

Measurements

The ^{1}H and ^{13}C NMR spectra were measured 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.[17-19] 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. Differential scanning

calorimetric (DSC) carves were obtained with a DSC 50 (Shimadzu Co.) under nitrogen

at a heating rate of 10°C/min. Thermogravimetry (TG) was performed on a TGA-50

(Shimadzu Co.) apparatus under nitrogen flow (20 mL/min) at a heating rate of 10°C/min.

The transmittance of a poly(NIPAAm) solution (0.1 w/v%) was monitored at 500nm as a

function of temperature with an UV-spectrophotometer (V-550 (JASCO Co.)). The

temperature was changed at 0.5 °C/min. The cloud point (T_c) was defined as the

temperature at which the transmittance is 50% in heating and cooling processes.

RESULTS AND DISCUSSION

Radical Polymerization of NIPAAm in the Presence of Alcohol Compounds

First, we carried out radical polymerization of NIPAAm in toluene at –40°C in the

presence of a fourfold amount of alkyl alcohol compounds, such as MeOH, EtOH, i-PrOH,

t-BuOH, and 3Me3PenOH, to investigate the effect of alcohol compounds on the

stereospecificity of NIPAAm polymerization (Table 1, runs 3, 8, 11, 12, 15, and 20).

Adding alkyl alcohols significantly induced syndiotactic-specificity, and the magnitude

was enhanced with the bulkiness of the added alcohols. This result indicates that alkyl

alcohols have an efficient stereocontrolling power in the radical polymerization of

NIPAAm as well as NVA. It should be noted that the added alkyl alcohols induced

opposite stereospecificity in the polymerization of NVA and NIPAAm.[27]

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<Table 1>

Thus, we investigated the temperature effect on the syndiotactic-specificity in the radical polymerization in the presence of MeOH (Table 1, runs 6-10), *t*-BuOH (Table 1, runs 13-17), or 3Me3PenOH (Table 1, runs 18-22). Polymers were quantitatively obtained with the addition of any examined alcohols irrespective of polymerization temperature, whereas polymer yield slightly reduced with a decrease in polymerization temperature in the absence of alcohol compounds. Molecular weights of the polymers obtained in the presence of alcohol compounds gradually increased with a decrease in polymerization temperature, whereas those in the absence of alcohol compounds gradually decreased. The effect of alcohol compounds on the polymer yield will be discussed later.

Figure 1 shows relationship between polymerization temperature and *r* diad content of the obtained poly(NIPAAm)s. The syndiotacticity slightly increased by lowering temperature and the tendency was enhanced with the bulkiness of the added alcohol. Maximum syndiotacticities were observed around –60°C. In particular, the *r* diad content reached up to 71% at –60°C in the presence of 3Me3PenOH. These results indicate that, in NIPAAm polymerization, bulky alkyl alcohols such as 3Me3PenOH exhibit significant stereocontrolling power comparable to HMPA, which has afforded the highest syndiotacticity among those of the radically prepared poly(NIPAAm)s so far reported.[21,23,24]

<Figure 1>

Next, we examined effect of the added amount of alcohol compounds on the syndiotactic-specificity in NIPAAm polymerization at –40°C (Table 2).[28] Figure 2 demonstrates relationship between the $[3Me3PenOH]_0$ / $[NIPAAm]_0$ ratio and r diad content of the obtained poly(NIPAAm)s. The syndiotacticity gradually increased with the $[3Me3PenOH]_0$ / $[NIPAAm]_0$ ratio and became almost constant over the ratio = 2, whereas the addition of catalytic amount of 3Me3PenOH hardly influenced the stereospecificity. This result suggests that at least a twofold amount of alcohols is required in order to significantly induce the syndiotactic-specificity in this polymerization system.

<Table 2>

<Figure 2>

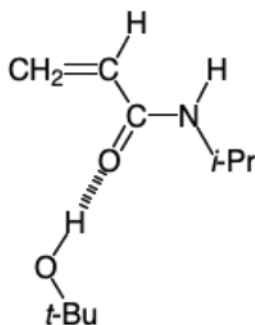**Hydrogen-Bonding Interaction between NIPAAm and Alcohol Compounds**

To confirm the concernment of a hydrogen-bonding interaction to the stereocontrol in NIPAAm polymerizations, we conducted NMR analysis of mixture of NIPAAm and t-BuOH (Figures 3 and 4),[29] in which the concentration of NIPAAm was kept at 0.2 mol/L. Some signals significantly shifted by changing the added amount of t-BuOH.

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<Figure 3>

<Figure 4>

The chemical shift of signal due to –OH proton of t-BuOH alone also varies with concentration, because t-BuOH associates with itself through a hydrogen-bonding interaction. Thus, the differences in chemical shift of –OH proton of t-BuOH [$\Delta\delta$(-OH)] between the signals of the sample and t-BuOH alone at corresponding concentrations were plotted to the [t-BuOH]$_0$ / [NIPAAm]$_0$ ratio, as shown in Figure 5a. Figures 5b and 5c display the changes in chemical shift of –NH proton of NIPAAm [$\Delta\delta$(-NH)] and of C=O carbon of NIPAAm [$\Delta\delta$(C=O)], respectively, with the [t-BuOH]$_0$ / [NIPAAm]$_0$ ratio. The signals due to –OH proton of t-BuOH showed downfield shifts by mixing with NIPAAm regardless of concentration of t-BuOH (Figure 5a). Furthermore, the signals due to C=O carbon of NIPAAm also exhibited slight downfield shift with an increase in the added amount of t-BuOH (Figure 5c). These results indicate that NIPAAm and t-BuOH form a hydrogen-bonding interaction between –OH proton of t-BuOH and C=O oxygen of NIPAAm as shown below.

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<Figure 5>

On the other hand, the signals due to –NH proton of NIPAAm showed slight upfield shift at low $[t\text{-BuOH}]_0 / [\text{NIPAAm}]_0$ ratio, but changed into downfield shift in the presence of excess amounts of t-BuOH (Figure 5b). This means that alcohol compounds behave as not only proton donor but also proton acceptor like in the case of NVA polymerization[27]; NIPAAm and t-BuOH also form a hydrogen-bonding interaction between –NH proton of NIPAAm and -OH oxygen of t-BuOH at high $[t\text{-BuOH}]_0 / [\text{NIPAAm}]_0$ ratio, probably because of a cooperative effect by C=O ••• H-O hydrogen bond (Scheme 1).[30] Taking into account that syndiotactic-specificity gradually increased as the $[\text{3Me3PenOH}]_0 / [\text{NIPAAm}]_0$ increased until 2, the alcohol compounds coordinating to –NH proton should attribute to the induction of syndiotactic-specificity in this polymerization system. This corresponds with the mechanism for HMPA-mediated syndiotactic-specific polymerization of NIPAAm, in which we proposed that the syndiotactic-specificity is induced by the steric interaction between HMPAs coordinating to –NH protons of NIPAAm monomer and the propagating chain-end.[17]

<Scheme 1>

It has been reported that, in radical polymerization of NIPAAm in water, an increase in $[\text{M}]_0$ results in a decrease in apparent propagation rate coefficient (k_p), probably due to strong aggregation of monomers and/or polymers.[31] Although both

Lewis bases and alcohol compounds should dissociate such aggregations, polymers were quantitatively obtained in the presence of alcohols and, on the contrary, an obvious retardation was observed in the presence of HMPA (cf. Table 1, run 23). This result suggests that hydrogen-bond-assisted complex formation also changed the reactivity of NIPAAm monomer. Based on the quantitative yield in the presence of alcohol compounds, it is assumed that alcohol compounds accelerate the polymerization reaction. Thus, we examined the acceleration effect of alcohol compounds by reducing initiator concentration (0.01 mol/L) and shortening polymerization time (10min) at 0°C (Table 1, Runs 24 and 25). The both polymerization systems proceeded homogeneously and the polymer yield pronouncedly increased by adding 3Me3PenOH, as expected.

Hatada et al. have reported that, among homologous monomers such as acrylates, methacrylates, and substituted styrenes, the chemical shift difference between α- and β-carbons in vinyl groups decreases with an increase in Q-value.[32] The signals due to α- and β-carbons of NIPAAm exhibited slight upfield and slight downfield shifts, respectively, by adding t-BuOH (Figures 3 and 6), resulting in a decrease in the chemical shift difference. In contrast, the chemical shift difference between α- and β-carbons of NIPAAm increased with the addition of HMPA (Figure 6). These results suggest that resonance stabilization in CH_2=CH-C=O moiety of NIPAAm is enhanced by the alcohol compound which forms hydrogen bond with carbonyl group of NIPAAm, taking into account that hydrogen bond formation between C=O and –OH significantly enhances k_p in radical polymerization of α,β-unsaturated ester monomers.[33] Therefore, it is assumed that the added alcohol compounds not only induced the syndiotactic-specificity by

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coordinating to –NH proton but also accelerated polymerization reaction by coordinating to C=O oxygen in the radical polymerization of NIPAAm, although precise kinetic analysis of elementary reactions such as propagating and terminating reactions is required to predicate the acceleration effect.

<Figure 6>

Properties of syndiotactic poly(NIPAAm)s

<u>Thermal properties</u>

It is known that degradation behavior[34] and glass transition temperature (T_g)[35] of poly(methyl methacrylate) strongly depend on both tacticity and molecular weight. Thus, to examine the effect of syndiotacticity and molecular weight on thermal degradation and T_g of poly(NIPAAm), we conducted TG and DSC measurements of poly(NIPAAm) with r diad content of 53-71% (cf. Table 1, Runs 1, 6, 18, and 22), of which number-average molecular weights lie in $2.55 \times 10^4 \sim 8.87 \times 10^4$ g/mol. Poly(NIPAAm)s exhibited similar degradation behavior regardless of the syndiotacticity and molecular weight: all the poly(NIPAAm)s examined degraded in a single step around 330-440°C and the maximal degradation rate was observed around 420°C. On the contrary, the T_g of poly(NIPAAm)s almost linearly increased with r diad content of poly(NIPAAm)s (Figure 7), although the T_g of poly(NIPAAm) with $r = 60\%$ slightly deviated below probably due to its low molecular weight. These results suggest that syndiotacticity hardly influences degradation behavior but significantly increases T_g of poly(NIPAAm) in at least this

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molecular weight range.

<Figure 7>

Phase transition behavior

Poly(NIPAAm) is one of representative polymers which exhibit a lower critical solution temperature (LCST).[36] Recently, it was reported that an increase in isotacticity gradually reduced the LCST of poly(NIPAAm) and poly(NIPAAm)s with m diad over 72% were changed into insoluble in water, whereas atactic poly(NIPAAm) shows phase transition around 32°C.[37] This result indicates that tacticity strongly influences the solution property of poly(NIPAAm). Thus, we examined the effect of syndiotacticity on the phase transition of poly(NIPAAm) solutions.

Figure 8 shows the temperature dependences of transmittance of aqueous solution of poly(NIPAAm)s with r diad content of (a) 53% and (b) 71%, respectively. In contrast to isotactic poly(NIPAAm)s, the T_c in heating process slightly increased from 33.1°C to 35.9°C with an increase in r diad content of poly(NIPAAm) from 53% to 71%. Furthermore, syndiotactic poly(NIPAAm) exhibited a smaller hysteresis between heating and cooling processes and sharper phase transition than atactic polymer.

<Figure 8>

Next, we examined the effect of methanol on the phase transition, because an

addition methanol decreases the LCST of poly(NIPAAm) solutions.[36a,38] Figure 9 demonstrates the temperature dependences of transmittance of methanol/H_2O solutions of poly(NIPAAm)s having $r = 53\%$ and $r = 71\%$. The phase transition temperature decreased with increasing methanol content regardless of tacticity. However, syndiotactic poly(NIPAAm) exhibited sharp phase transition even at higher methanol content (Figures 9c and 9d), although the phase transition of atactic pol(NIPAAm) further broadened as the methanol content increased (Figures 9a and 9b). These results indicate that an increase in the syndiotacticity improves sensitivity of the characteristic phase transition behavior of poly(NIPAAm).

<Figure 9>

CONCLUSION

We succeeded in inducing syndiotactic-specificity and accelerating reaction by adding simple alkyl alcohols into radical polymerization of NIPAAm. With the aid of NMR analysis, it was revealed that alcohol compounds coordinating to –NH proton induced the syndiotactic-specificity and alcohol compounds hydrogen-bonded with C=O oxygen accelerated the polymerization reaction. Taking into account that syndiotactic-specificity was significantly induced by just adding simple alkyl alcohol, quite safer than HMPA, under air, the methodology described in this paper provides one of the most promising ways for industrial production of stereoregular polymers via radical polymerization. Moreover, it appeared that the increase in syndiotacticity affected the properties of

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poly(NIPAAm). In particular, both temperature and sensitivity of phase transition

behavior of poly(NIPAAm) solutions were successfully controlled. Further work is now

under way to examine effect of fluoroalcohols in addition to further bulkier alkyl alcohol

on the stereospecificity of NIPAAm polymerization.

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28. Polymerizations were conducted at –40°C, because polymerization reaction proceeded heterogeneously below –40°C even in the presence of a fourfold amount of alcohol compounds.

29. *t*-BuOH was selected as an alcohol compound to simplify the spectra of mixtures of NIPAAm and alcohol compound.

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Table 1. Radical polymerization of NIPAAm in toluene for 24h at various temperatures in the absence or presence of a fourfold amount of simple alcohols[a]

Run	Alcohol	Temp. °C	Yield %	Tacticity / %[b] m	Tacticity / %[b] r	$M_n{}^c$ x 10^4	$M_w{}^c$ / M_n
1[d]	None	0	96	46	53	4.07	1.6
2[d]	None	-20	97	48	52	3.65	1.8
3[d]	None	-40	89	46	54	2.72	1.8
4[d]	None	-60	49	47	53	2.44	1.6
5[d]	None	-80	70	46	54	2.70	1.7
6	MeOH	0	96	40	60	2.55	1.6
7	MeOH	-20	95	38	62	1.98	1.3
8	MeOH	-40	98	38	62	2.44	1.3
9	MeOH	-60	>99	37	63	2.88	1.3
10	MeOH	-80	>99	38	62	5.22	1.3
11	EtOH	-40	86	36	64	3.76	1.3
12	i-PrOH	-40	92	36	64	2.87	1.3
13	t-BuOH	0	>99	35	65	4.95	1.5
14	t-BuOH	-20	>99	34	66	3.57	1.4
15	t-BuOH	-40	99	33	67	4.01	1.5
16[d]	t-BuOH	-60	99	33	67	5.27	1.3
17[d]	t-BuOH	-80	>99	33	67	2.76	1.4
18	3Me3PeOH	0	>99	36	64	5.49	1.4
19	3Me3PeOH	-20	>99	32	68	6.00	1.4
20	3Me3PeOH	-40	>99	31	69	5.88	1.5
21[d]	3Me3PeOH	-60	>99	29	71	8.87	1.5
22[d]	3Me3PeOH	-80	>99	30	70	6.63	1.5
23[e]	HMPA	-40	18	34	66	2.40	1.4
24[f]	None	0	55	47	53	5.85	2.4
25[f]	3Me3PenOH	0	94	35	65	6.87	2.1

a. $[NIPAAm]_0 = 0.5$ mol/L, $[R\text{-}OH]_0 = 2.0$ mol/L, $[n\text{-}Bu_3B]_0 = 0.05$ mol/L.

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

c. Determined by SEC (polystyrene standards).

d. Monomer, polymer or both were precipitated during a polymerization reaction.

e. $[HMPA]_0 = 2.0$ mol/L.

f. $[n\text{-}Bu_3B]_0 = 0.01$ mol/L, polymerization time 10min.

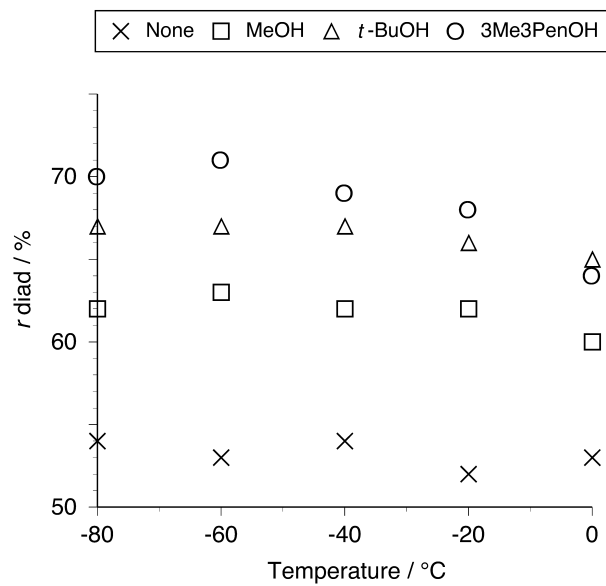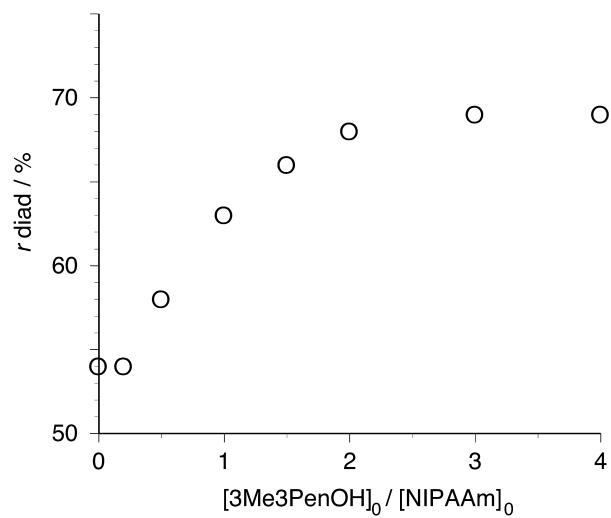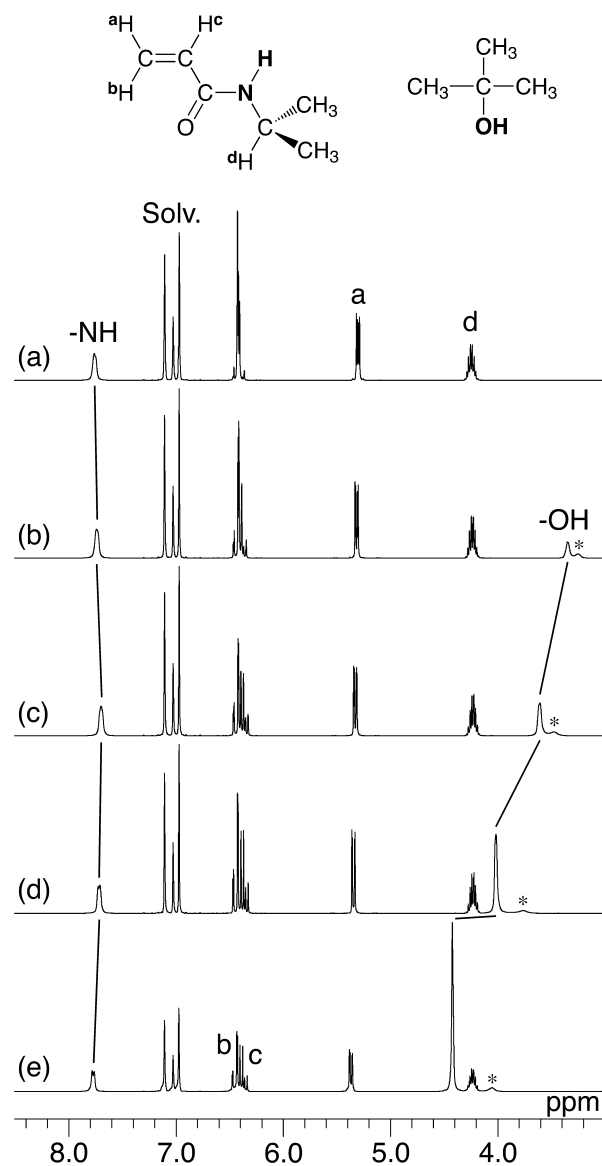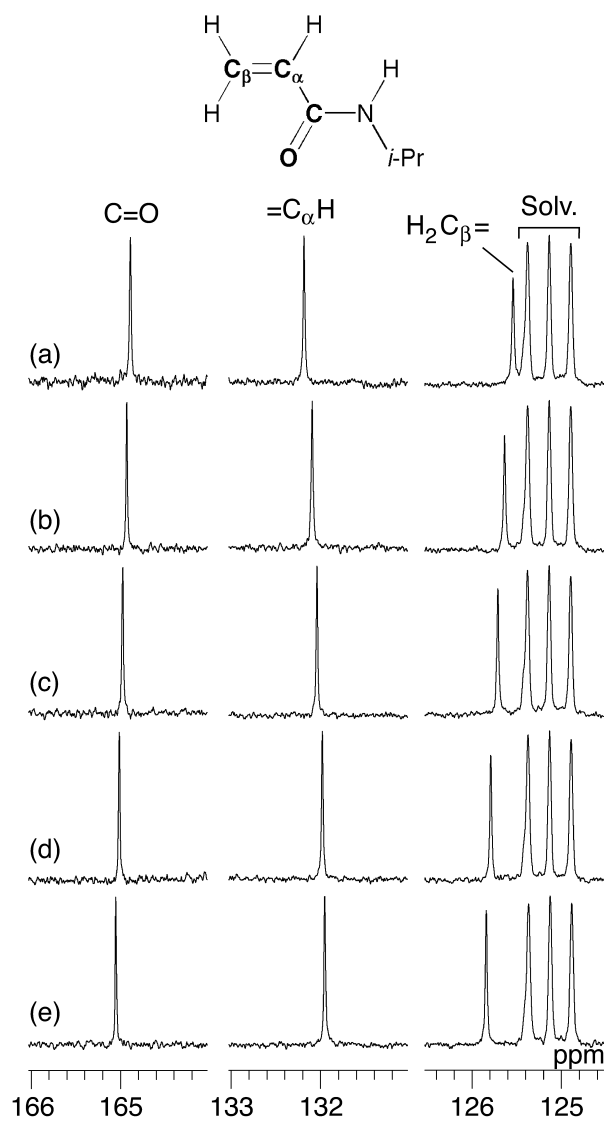Table 2. Radical polymerization of NIPAAm in toluene for 24h at –40°C in the presence of various amounts of 3Me3PenOH[a]

Run	$[\text{3Me3PenOH}]_0$ mol/L	Yield %	Tacticity / %[b] m	r	M_n[c] x 10^4	$\dfrac{M_w}{M_n}$[c]
1[d]	0.10	95	46	54	5.89	1.5
2[d]	0.25	>99	42	58	6.74	1.3
3	0.50	>99	37	63	7.17	1.4
4	0.75	>99	34	66	7.34	1.5
5	1.00	93	32	68	10.82	1.2
6	1.50	97	31	69	6.22	1.3

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

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

c. Determined by SEC (polystyrene standards).

d. Monomer, polymer or both were precipitated during a polymerization reaction.

Figure 1. Relationship between the polymerization temperature and r diad content of poly(NIPAAm)s prepared in the absence or presence of MeOH, t-BuOH, and 3Me3PenOH.

Figure 2. Relationship between the $[3Me3PenOH]_0$ / $[NIPAAm]_0$ ratio and r diad content of poly(NIPAAm)s prepared at –40°C.
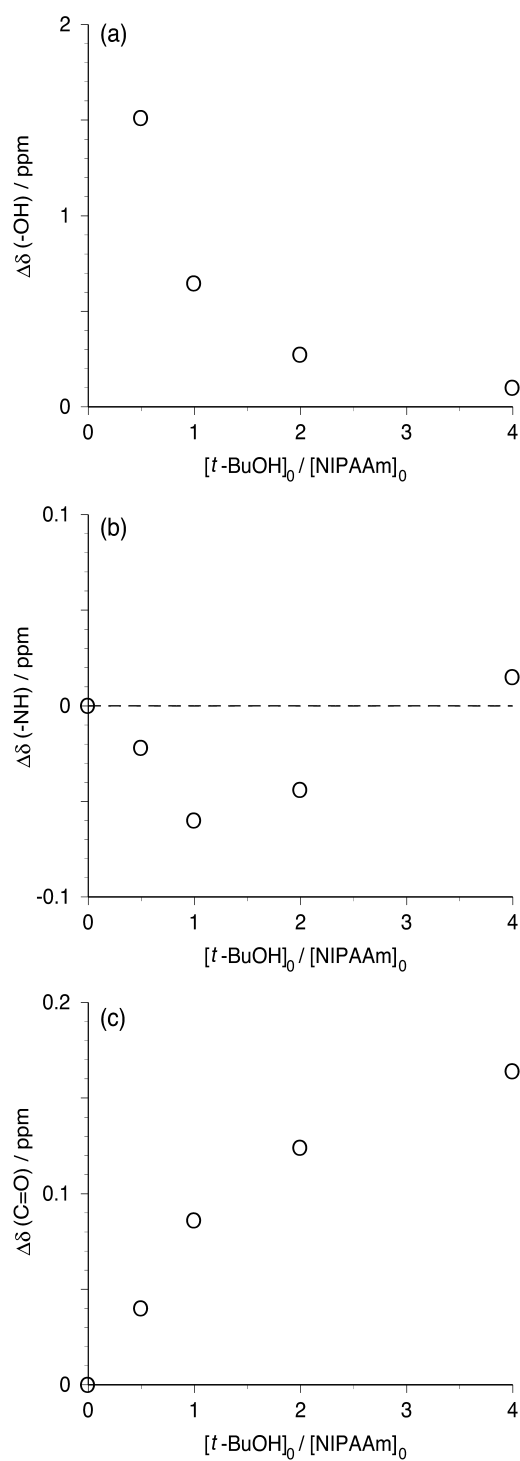
Figure 3. Expanded ^{1}H NMR spectra of NIPAAm ([NIPAAm]$_0$ = 0.2 mol/L) in the absence or presence of *t*-BuOH, as measured in toluene-d_8 at –20°C; [*t*-BuOH]$_0$ = (a) 0, (b) 0.1, (c) 0.2, (d) 0.4, and (e) 0.8 mol/L, respectively. * denotes contaminous H_2O.
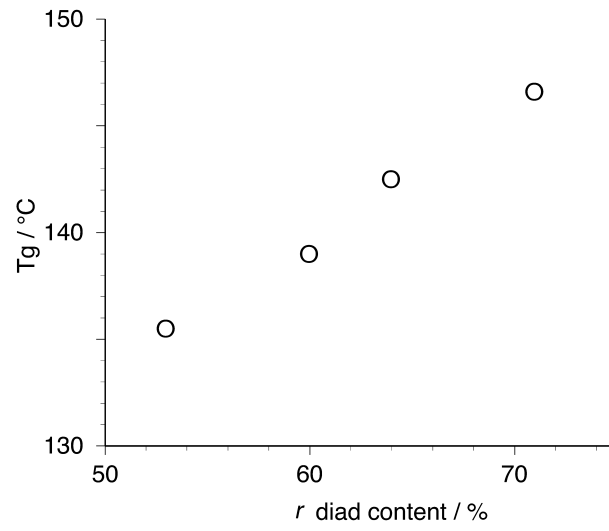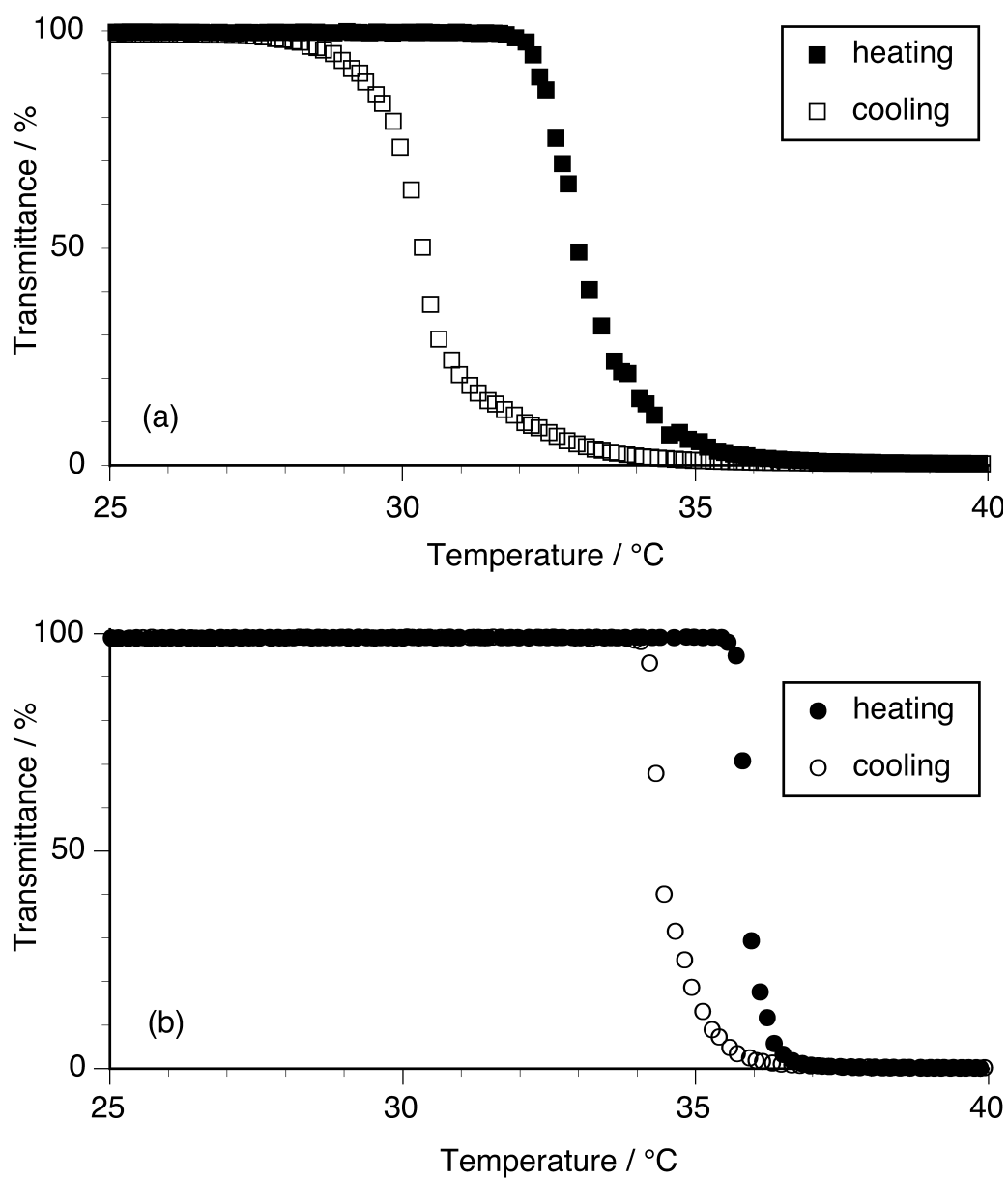
Figure 4. Expanded ^{13}C NMR spectra of NIPAAm ($[NIPAAm]_0$ = 0.2 mol/L) in the absence or presence of t-BuOH, as measured in toluene-d_8 at $-20°C$; $[t$-BuOH$]_0$ = (a) 0, (b) 0.1, (c) 0.2, (d) 0.4, and (e) 0.8 mol/L, respectively.

Figure 5. (a) Relationship between the $[t\text{-BuOH}]_0$ / $[\text{NIPAAm}]_0$ ratio and the ^{1}H NMR chemical shift difference of –OH proton of t-BuOH between the sample mixture and t-BuOH alone at corresponding concentrations and the changes in (b) ^{1}H NMR chemical shift of –NH proton and (c) ^{13}C NMR chemical shift of C=O carbon of NIPAAm monomer with the addition of t-BuOH.
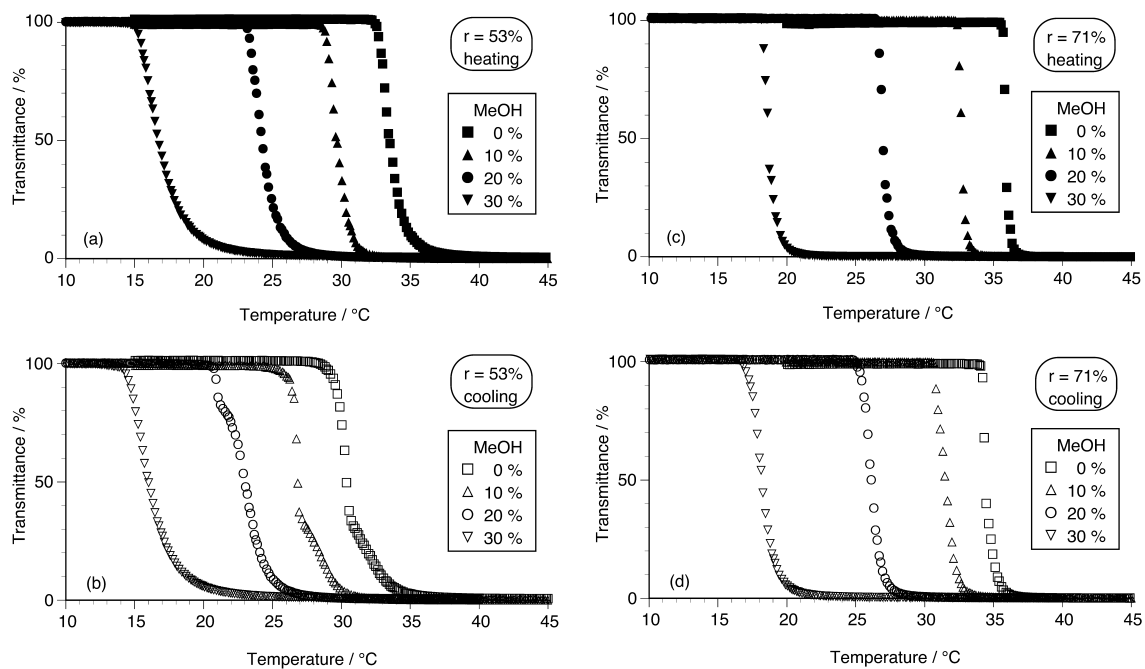
Figure 6. Expanded ^{13}C NMR spectra of carbonyl and vinyl carbons of NIPAAm monomer ([NIPAAm]$_0$ = 0.2 mol/L) in the absence or presence of t-BuOH and HMPA, as measured in toluene-d_8 at –20°C; (a) None, (b) [t-BuOH]$_0$ = 0.2 mol/L, and (c) [HMPA]$_0$ = 0.2 mol/L, respectively.
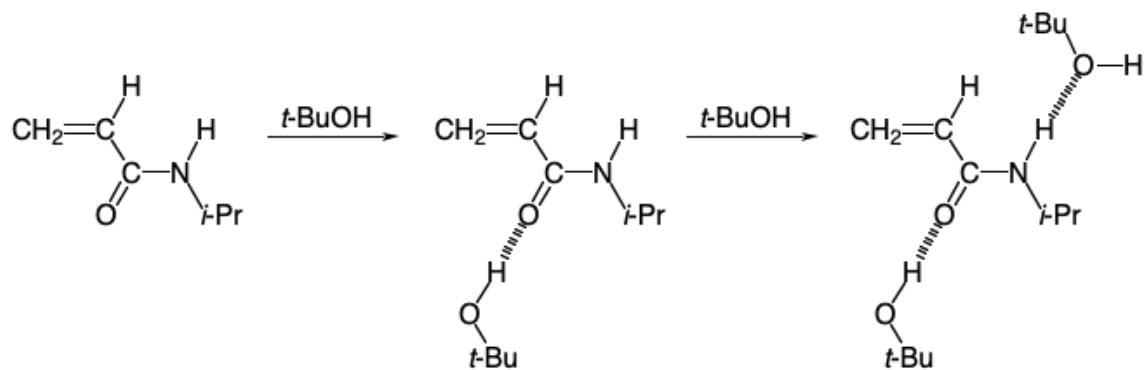
Figure 7. Relationship between T_g and r diad content of poly(NIPAAm)s.

Figure 8. Temperature dependence of the light transmittance (500nm) of the aqueous solutions of (a) atactic poly(NIPAAm) with $r = 53\%$ and (b) syndiotactic poly(NIPAAm) with $r = 71\%$ (0.1 w/v%, heating and cooling rates = 0.5 °C/min).

Figure 9. Effect of methanol on temperature dependence of the light transmittance (500nm) of atactic poly(NIPAAm) (r = 53%) [(a) heating and (b) cooling processes] and syndiotactic poly(NIPAAm) (r = 71%) [(c) heating and (d) cooling processes] (0.1 w/v%, heating and cooling rates = 0.5 °C/min).

Scheme 1. Schematic representation for formation of the hydrogen-bond-assisted complexes between NIPAAm monomer and *t*-BuOH.