Remarkable effect of hydrogen-bonding interaction on stereospecificity in the radical polymerization of *N*-vinylacetamide

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Abstract

Radical polymerization of *N*-vinylacetamide (NVA) in toluene at low temperatures was investigated. It was found that the addition of Lewis bases or alcohol compounds significantly influenced stereospecificity in NVA polymerization. For example, syndiotacticity increased from 25% to 34% by adding tri-*n*-butyl phosphate at –40°C. Mono-alcohol compounds increased heterotacticity and heterotactic poly(NVA) with *mr* triad content of 58% was obtained at –40°C in the presence of 1,1,1,3,3,3-hexafluoro-2-propanol. Furthermore, isotactic poly(NVA) with *mm* triad = 49% was obtained at –60°C in the presence of diethyl L-tartrate. The NMR analysis demonstrated that complex formation between NVA monomer and the added agents, through hydrogen-bonding interaction, played an important role to induce the stereospecificity.

Keywords: hydrogen bond; *N*-vinylacetamide; stereospecific radical polymerization; syndiotactic; heterotactic; isotactic;

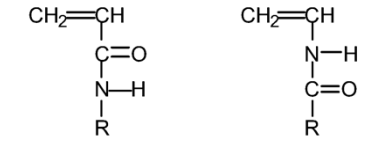
1. Introduction

It is well known that poly(*N*-isopropylacrylamide) [poly(NIPAAm)] shows a lower critical solution temperature (LCST) around 32°C [1-4]. Although stereostructures of macromolecules often affect their properties, the syntheses of stereoregular poly(NIPAAm)s were not reported until quite recently. Kitayama et al. reported that an anionic polymerization of trimethylsilyl-protected NIPAAm derivative with *t*-C_4H_9Li / *n*-$(C_4H_9)_3Al$ in toluene at –40°C followed by deprotection gave an isotactic poly(NIPAAm) with *meso* (*m*) diad content of 97% [5]. Okamoto et al. found that a radical polymerization of NIPAAm in methanol at –20°C in the presence of rare-earth metal trifluoromethanesulfonates (triflates) such as yttrium triflate gave directly an isotactic poly(NIPAAm) with *m* diad content of 92% [6,7]. Ishizone et al. reported that an anionic polymerization of *N*-isopropyl-*N*-methoxymethylacrylamide with alkyllithium / diethylzinc followed by deprotection provided syndiotactic poly(NIPAAm) with *racemo* (*r*) diad content of 75% [8]. It appeared that the LCST of poly(NIPAAm) gradually decreased with an increase in isotacticity and poly(NIPAAm)s with *m* diad over 72% were changed into insoluble in water, although atactic poly(NIPAAm) are one of representative water-soluble polymers [9]. These results indicate that the isotacticity strongly influences the solubility of poly(NIPAAm).

Recently, we have found that a hydrogen-bonding interaction is available to control the stereospecificity of radical polymerization of NIPAAm [10-16]. For instance, the addition of a fourfold amount of primary alkyl phosphates such as tri-*n*-butyl phosphate (TBP) produced isotactic poly(NIPAAm) with *m* diad of 57% at –80°C, whereas syndiotactic poly(NIPAAm)s were obtained at –40 to 0°C under the same conditions [11]. Furthermore, radical polymerization of NIPAAm in toluene in the presence of hexamethylphosphoramide (HMPA) afforded syndiotactic poly(NIPAAm)s regardless of temperature and the syndiotacticity reached up to 72% at

diad level by adding a fivefold amount of HMPA at –60°C [12,13]. It was found that fractionated syndiotactic poly(NIPAAm) with *r* diad of 75% exhibited an unusual hysteresis in transmittance analysis of an aqueous solution, although atactic poly(NIPAAm) shows reversible LCST around 32°C [13]. This result confirms that the syndiotacticity also affects the solubility of poly(NIPAAm).

N-Vinylalkylamides are structural isomers of *N*-alkylacrylamides [17-24]. Poly(*N*-vinyl-*n*-butyramide) and poly(*N*-vinylisobutyramide) also exhibit LCST as well as poly(NIPAAm) [20]. Furthermore, radical copolymerizations of *N*-vinylalkylamides having different hydrophobicities have been investigated and the LCST was successfully controlled [20-24]. However, there are no reports that put the focus on the stereoregularity of poly(*N*-vinylalkylamide)s. Thus, we started investigating the effect of hydrogen-bonding interaction to control the stereospecificity of radical polymerization of *N*-vinylacetamide (NVA), although poly(NVA)s does not exhibit any LCST. Here, we report that the hydrogen-bonding interaction also significantly affected the stereospecificity of NVA polymerization.



N-alkylacrylamide *N*-vinylalkylamide

2. Experimental

2.1. Materials

NVA (Aldrich Chemical 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. Tri-*n*-butylborane (*n*-Bu_3B) as a THF solution (1.0M), HMPA, triisopropyl phosphate (T*i*PP) (Aldrich Chemical Co.), trimethyl phosphate (TMP),

triethyl phosphate (TEP), TBP, isopropyl alcohol (*i*PrOH), *t*-butyl alcohol (*t*BuOH), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), diethyl L-tartrate (L-EtTar), diethyl D-tartrate (D-EtTar), diisopropyl tartrate (L-*i*PrTar), and di-*n*-butyl tartrate (L-BuTar) (Tokyo Kasei Kogyo Co.) were commercially obtained and used without further purification for polymerization reaction.

2.2. Polymerization

Typical polymerization procedure is as follows; NVA (0.449g, 5.3 mmol) was dissolved in toluene to prepare the 10 mL solution of 0.53 mol/L. Eight 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 48h, 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 acetone, and the precipitated polymer was collected by filtration or centrifugation, and dried *in vacuo*. The polymer yield was determined gravimetrically.

2.3. Measurements

The ^{1}H and ^{13}C NMR spectra of NVA monomer and/or added agents were measured in toluene-d_8 at desired temperatures on an EX-400 spectrometer (JEOL Ltd.) operated at 400MHz for ^{1}H and at 100MHz for ^{13}C. The triad tacticities of the poly(NVA)s were determined from ^{1}H NMR signals due to methyl group in the side chain, measured in D_2O at 25°C [19]. The molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography (SEC) (SC-8020 + RI-8020 (Tosoh Co.)) equipped with Shodex OHpak SB-8025HQ and Shodex OHpak SB-8026HQ (Showa Denko KK) using phosphate buffer solution (pH 7.4) as an eluent at 45°C. The SEC chromatogram was calibrated with standard

poly(ethylene oxide) samples.

3. Results and Discussion

3.1. Radical Polymerization of NVA in the Presence of Phosphoric Acid Derivatives

Table 1 summarizes the results of radical polymerization of NVA with *n*-Bu_3B in toluene in the absence or presence of phosphoric acid derivatives. In the absence of Lewis bases, the polymer yield drastically decreased with a decrease in temperature, whereas polymerization proceeded quantitatively at 0°C (Table 1, Runs 1-3). It is probably because NVA is classified as a nonconjugated type vinyl monomer [19]. The addition of Lewis bases, in particular HMPA, drastically decreased the polymer yield even at 0°C (Table 1, Runs 4-20).

Figure 1 displays the expanded ^{1}H NMR spectra of methyl group of the obtained poly(NVA). The resonances showed splittings due to triad tacticity as reported in the literature [19]. Thus, we determined triad tacticity from the signal due to methyl group. The addition of Lewis bases slightly increased the syndiotacticity of the obtained poly(NVA)s. The syndiotacticity increased with the added amount of Lewis bases. These results correspond to the results observed in NIPAAm polymerization in the presence of the added Lewis bases [10-12,14]. The syndiotacticity reached up to *rr* triad content of 34% (Figure 1b) by lowering temperature to –40°C in the presence of a fourfold amount of TBP.

<Table 1>

<Figure 1>

Figure 2 demonstrates the relationship between the parameters of the first order Markovian statistics and the $[\text{Lewis base}]_0$ / $[\text{NVA}]_0$ ratio. The parameter P*r*/*m* denotes the probability of *m*-addition by *r*-ended radical (~~~*rM*•) and the parameter

P*m*/*r* denotes that of *r*-addition by *m*-ended radical (~~~*mM*•). By adding Lewis bases, both values slightly decreased as compared with those in the absence of Lewis bases. This means that *r*-selectivity of *m*-ended radical slightly decreased, whereas *r*-selectivity of *r*-ended radical slightly increased. Thus, such opposite effects of Lewis base on the stereoselectivity of ~~~*mM*• and ~~~*rM*• seemed to result in a slight increase in the syndiotacticity of the obtained poly(NVA)s.

The reason why *r*-selectivity of *m*-ended radical slightly decreased with the coordination by Lewis bases is not clear at this time. But, it is assumed that *m*-ended radical selectively changed the conformation near the chain-end and hence *m*-selectivity increased, like in the case of isotactic-specific radical polymerization of triphenylmethyl methacrylate [25], because steric repulsion between the Lewis bases coordinating to penultimate and antepenultimate monomeric units of *m*-ended radical must be larger than that of *r*-ended radical.

<Figure 2>

3.2. Radical Polymerization of NVA in the Presence of Alcohol Compounds

It is known that the use of perfluoroalcohol as a solvent induced stereospecificities in polymerizations of methacrylates [26-28] and vinyl esters [29], the latter of which are also classified as nonconjugated type monomers. Thus, we conducted polymerization of NVA in the presence of alcohol compounds instead of phosphoric acid derivatives (Table 2). The addition of alcohols also reduced the polymer yield and the effect was enhanced with the added amount of alcohols, although the yield in the presence of MeOH and EtOH somewhat scattered. The syndiotacticity decreased and both the isotacticity and the heterotacticity increased by adding simple alkyl alcohols (Table 2, Runs 1-15), in contrast to the cases of phosphoric acid derivatives. This result contrasted with the fact that simple alkyl alcohol hardly

affected the stereospecificity of radical polymerization of vinyl esters [29]. The magnitude of the reduced syndiotacticity increased with both the added amount and the bulkiness of alcohols. However, significant temperature-dependence of the stereospecificity was not observed for NVA polymerization in the presence of *t*-BuOH (Table 2, Runs 12-15).

Then we added HFIP as a fluoroalcohol (Table 2, Runs 16-20). The syndiotacticity decreased and the heterotacticity increased, whereas the isotacticity were almost constant. Lowering temperature enhanced the tendency (Table 2, Runs 18-20). The *mr* triad tacticity reached up to 58% by lowering temperature to –40°C in the presence of a fourfold amount of HFIP (Figure 1c). It should be noted that there are limited reports on the preparation of heterotactic polymers by radical polymerization [29-31].

Figure 3 displays the relationship between parameters of the first order Markovian statistics and the ratio of $[Alcohol]_0$ / $[NVA]_0$. In the presence of simple alkyl alcohols, the parameter P*r*/*m* gradually increased with the $[Alcohol]_0$ / $[NVA]_0$ ratio, whereas the parameter P*m*/*r* slightly decreased with the ratio. This means that *m*-selectivity of ~~~*rM*• favorably increased, whereas *r*-selectivity of ~~~*mM*• slightly decreased. On the other hand, in the presence of HFIP, the parameter P*r*/*m* slightly increased with the $[HFIP]_0$ / $[NVA]_0$ ratio, whereas the parameter P*m*/*r* was hardly affected by the ratio. This means that only the *r*-selectivity of ~~~*rM*• selectively increased by the addition of HFIP.

<Table 2>

<Figure 3>

3.3. Radical Polymerization of NVA in the Presence of Diol Compounds

Next, we examined the effect of diol compunds on the stereospecificity of

NVA polymerization (Table 3). L-Tartrates were chosen as diol compounds, because an enhancement of the isotactic-specificity by the chirality was expected. Unlike mono-alcohol compounds, poly(NVA)s were quantitatively obtained except for lower temperatures. With a decreased in temperature, not only did the syndiotacticity decrease, but also a significant increase in the isotacticity was observed. The isotacticity increased as the bulkiness of ester groups decreased. The isotacticity reached up to *mm* = 49% at –60°C in the presence of a twofold amount of L-EtTar (Figure 1d).

To examine effect of the chirality of the added tartrates on the stereospecificity, we added diethyl *racemic*- and D-tartrates to the polymerization at –60°C (Table 3, Runs 5 and 6). Not only D-EtTar but also *rac*-EtTar afforded poly(NVA)s having almost the same tacticities as that of poly(NVA) formed in the presence of L-EtTar (Table 3, Run 4). This suggests that the induced isotactic-specificity was not ascribed to the chirality but the diol structure.

Significant effect of the temperature on the stereoselectivities of the propagating radicals were observed; *m*-selectivities of both ~~~*mM*• and ~~~*rM*• increased as the temperature decreased (Figure 4). These tendencies contrast with the results observed in the presence of mono-alcohol compounds (cf. Figure 3).

<Table 3>

<Figure 4>

3.4. Molecular Weights of the Obtained Poly(NVA)s

To evaluate number average molecular weight (M_n) and molecular weight distribution (M_w/M_n), we conducted SEC analysis of two samples among the obtained poly(NVA)s (sample **1**: Table 1, Run 1; sample **2**: Table 2, Run 12). M_n and M_w/M_n were estimated to be 8.4 x 10^3 and 2.65 for **1** and 5.5 x 10^3 and 2.95 for **2**, respectively.

The molecular weights of the poly(NVA)s were 5-10 times lower than those of poly(NIPAAm)s obtained under the corresponding conditions [11,14,16]. Such obvious decreased in molecular weight of poly(NVA)s could be explained by the following two reasons: (1) the reactivity of nonconjugated NVA is lower than that of conjugated NIPAAm and (2) electron rich radical in NVA polymerization would favor to abstract hydrogen atom from electron deficient methyl group adjacent to carbonyl group of NVA monomer, taking account of the small Q-value and the large negative e-value of NVA monomer [19].

3.5. Hydrogen-Bonding Interaction of NVA with the added reagents

To confirm the concernment of a hydrogen-bonding interaction to the stereocontrol in NVA polymerizations, we conducted NMR analysis of mixture of NVA and added agents. Figure 5 displays ^{1}H NMR spectra of (a) NVA (0.25 mol/L), (b) mixture of NVA and TBP ($[NVA]_0 = [TBP]_0 = 0.25$ mol/L), (c) mixture of NVA and *t*-BuOH ($[NVA]_0 = [t\text{-BuOH}]_0 = 0.25$ mol/L), and (d) *t*-BuOH (0.25 mol/L), as measured in toluene-d_8 at 0°C. The signal due to the amide proton exhibited downfield shift by adding TBP (Figures 5**a** and **b**). This means that NVA and TBP formed a complex through a hydrogen-bonding interaction as shown in Scheme 1, similar to the combination of NIPAAm and TBP [11]. In the spectrum of mixture of NVA and *t*-BuOH, the signals due to not only the amide proton of NVA (Figures 5**a** and **c**) but also the hydroxyl proton of *t*-BuOH (Figures 5**c** and **d**) shifted downfield in comparison with the spectrum of each component, although the signal due to hydroxyl proton overlapped with the solvent peak in the spectrum of *t*-BuOH. If *t*-BuOH behaves only as a proton donor, the signal due to amide proton should shift to upper magnetic field, because NVA monomer associates with itself through a hydrogen-bonding interaction between the amide proton and the carbonyl oxygen. Thus, it is suggested that *t*-BuOH behaved not only as a proton donor but also as a

proton accepter (Scheme 1).

<Figure 5>

Figures 6 and 7 display ^{1}H and ^{13}C NMR spectra of (a) NVA (0.25 mol/L), (b) mixture of NVA and L-EtTar ($[NVA]_0$ = 0.25 mol/L, $[L\text{-}EtTar]_0$ = 0.125 mol/L), (c) mixture of NVA and L-EtTar ($[NVA]_0$ = $[L\text{-}EtTar]_0$ = 0.25 mol/L), and (d) L-EtTar (0.25 mol/L), as measured in toluene-d_8 at 0°C. The signal due to hydroxyl protons of L-EtTar significantly shifted downfield by mixing with a twofold amount of NVA (Figures 6**b** and **d**). The signal showed a further downfield shift by mixing equimolar amounts of NVA and L-EtTar (Figures 6**b** and **c**). Moreover, the signal due to carbonyl group of NVA also shifted by adding L-EtTar (Figures 7**a**-**c**). These results indicate that L-EtTar formed a complex with NVA through a hydrogen-bonding interaction between hydroxyl group of L-EtTar and carbonyl group of NVA.

The signals due to amide proton of NVA and carbonyl group of L-EtTar also slightly shifted downfield by mixing NVA and L-EtTar (Figures 6**a**-**c** and 7**b**-**d**). These results suggest that weak hydrogen bonds were also formed with amide hydrogen of NVA and carbonyl group of L-EtTar.

Carbonyl carbon of L-EtTar showed single peaks regardless of the presence of NVA (Figures 7**b**-**d**). This indicates that L-EtTar kept the symmetric character even in the complex. Furthermore, the signals due to hydroxyl protons and methine protons of L-EtTar exhibited clear coupling, as evidenced by selective spin decoupling experiments (Figure 8) [32]. This means that the hydrogen-bonding interaction in the NVA-L-EtTar complex is so strong compared with that in other complexes such as the NVA-*t*-BuOH complex. Thus, based on the fact that dialkyl tartrates favor *trans* conformation with two O=C-C-OH synplanar bonds [33], it is assumed that L-EtTar and NVA formed a complex through hydrogen bonds between two hydroxyl groups of

L-EtTar and one carbonyl group of NVA (Scheme 2) [34] and the complex stabilized by double hydrogen bonding weakly interact each other through hydrogen-bonding interaction between amide group of NVA fragment and ester group of L-EtTar fragment.

<Figure 6>

<Figure 7>

<Figure 8>

4. Conclusions

The radical polymerization of NVA was investigated in the presence of phosphoric acid derivative or alcohol compounds. We succeeded in the stereocontrol of NVA polymerization; a slight increase in syndiotacticity with Lewis bases, a slight increase in heterotacticity with mono-alcohol compounds, and a significant increase in isotacticity with diol compounds. These results indicate that the proper selection of the added agents allows ones to control the stereospecificity even in radical polymerization of nonconjugated NVA. The NMR analysis demonstrated that a hydrogen-bonding interaction between NVA monomer and the added agents is the key of the induced stereospecificity. The structure of the hydrogen-bond-assisted monomer complex is now investigated in detail to reveal the mechanism of these stereospecific polymerizations and hence to achieve higher level of stereoregulation. Furthermore, polymerization of other monomers such as *N*-vinylisobutyramide is also in progress to examine the tacticity dependence of their phase-transition behaviors.

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Table 1.

Radical Polymerization of NVA in toluene for 48h in the presence of Lewis bases

Run	Lewis base	$[\text{Lewis base}]_0$	Temp. °C	Yield %	Triad tacticity/%[a] *mm*	*mr*	*rr*	P*m*/*r*[b]	P*r*/*m*[b]
1[c]	None	0.0	0	>99	22	53	25	0.55	0.51
2[c]	None	0.0	–20	83	21	53	26	0.56	0.51
3[c]	None	0.0	–40	1	24	53	23	0.53	0.53
4[c]	HMPA	0.5	0	9	25	47	28	0.48	0.46
5	HMPA	1.0	0	4	26	43	31	0.45	0.41
6	HMPA	2.0	0	trace	-	-	-	-	-
7[c]	TMP	0.5	0	70	21	53	26	0.56	0.50
8[c]	TMP	1.0	0	27	21	52	27	0.55	0.49
9[c]	TMP	2.0	0	22	19	49	31	0.56	0.44
10[c]	TEP	0.5	0	58	22	49	29	0.53	0.46
11[c]	TEP	1.0	0	51	21	50	29	0.54	0.46
12[c]	TEP	2.0	0	32	20	48	32	0.55	0.43
13[c]	T*i*PP	0.5	0	12	22	50	28	0.53	0.47
14[c]	T*i*PP	1.0	0	10	22	50	28	0.53	0.47
15[c]	T*i*PP	2.0	0	18	24	47	29	0.49	0.45
16[c]	TBP	0.5	0	22	21	53	26	0.56	0.50
17[c]	TBP	1.0	0	39	23	52	25	0.53	0.51
18[c]	TBP	2.0	0	43	23	48	29	0.51	0.45
19[c]	TBP	2.0	–20	3	21	46	33	0.52	0.41
20	TBP	2.0	–40	2	18	48	34	0.57	0.41

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

a. Determined by ^{1}H NMR signals due to methyl group.

b. Parameters of the first order Markovian statistics.

c. The monomer, polymer or both were precipitated during the polymerization reaction.

Table 2.

Radical Polymerization of NVA in toluene for 48h in the presence of alcohol compounds

Run	Alcohol	[Alcohol]$_0$	Temp. °C	Yield %	Triad tacticity/%[a] *mm*	*mr*	*rr*	P*m*/*r*[b]	P*r*/*m*[b]
1	MeOH	0.5	0	62	25	52	23	0.51	0.53
2	MeOH	1.0	0	27	27	53	20	0.50	0.57
3	MeOH	2.0	0	47	29	54	17	0.48	0.61
4	EtOH	0.5	0	46	28	52	20	0.48	0.57
5	EtOH	1.0	0	71	28	53	19	0.49	0.58
6	EtOH	2.0	0	17	34	51	15	0.43	0.63
7[c]	*i*-PrOH	0.5	0	74	28	53	19	0.48	0.58
8[c]	*i*-PrOH	1.0	0	73	27	54	19	0.51	0.60
9	*i*-PrOH	2.0	0	31	28	56	16	0.50	0.64
10	*t*-BuOH	0.5	0	69	27	53	20	0.50	0.58
11	*t*-BuOH	1.0	0	63	30	53	17	0.47	0.61
12	*t*-BuOH	2.0	0	60	30	57	13	0.49	0.69
13	*t*-BuOH	2.0	–20	18	33	56	11	0.46	0.72
14	*t*-BuOH	2.0	–40	7	32	57	11	0.47	0.72
15[c]	*t*-BuOH	2.0	–60	13	34	54	12	0.44	0.69
16	HFIP	0.5	0	98	25	53	22	0.52	0.55
17	HFIP	1.0	0	83	23	54	23	0.54	0.54
18	HFIP	2.0	0	48	23	56	21	0.54	0.57
19	HFIP	2.0	–20	43	24	58	18	0.55	0.62
20[c]	HFIP	2.0	–40	28	25	58	17	0.54	0.63

$[NVA]_0$ = 0.5 mol/L, $[n\text{-}Bu_3B]_0$ = 0.05 mol/L.

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

b. Parameters of the first order Markovian statistics.

c. The monomer, polymer or both were precipitated during the polymerization reaction.

Table 3.

Radical Polymerization of NVA in toluene for 48h in the presence of tartrates

Run	Tartrate	Temp.	Yield	Triad tacticity/%[a]			P*m*/*r*[b]	P*r*/*m*[b]
		°C	%	*mm*	*mr*	*rr*		
1	L-EtTar	0	>99	36	54	10	0.43	0.73
2	L-EtTar	–20	>99	39	52	9	0.40	0.74
3	L-EtTar	–40	>99	41	51	8	0.38	0.76
4	L-EtTar	–60	97	49	46	5	0.32	0.82
5	D-EtTar	–60	43	48	46	6	0.32	0.79
6	*rac*-EtTar	–60	49	47	47	6	0.33	0.80
7	L-*i*PrTar	0	>99	37	53	10	0.42	0.73
8	L-*i*PrTar	–20	>99	38	52	10	0.41	0.72
9	L-*i*PrTar	–40	>99	42	51	7	0.38	0.78
10	L-*i*PrTar	–60	89	43	51	6	0.37	0.81
11	L-BuTar	0	>99	34	53	13	0.44	0.67
12	L-BuTar	–20	97	36	54	10	0.43	0.73
13	L-BuTar	–40	76	41	49	10	0.37	0.71
14	L-BuTar	–60	87	42	51	7	0.38	0.78

$[NVA]_0$ = 0.5 mol/L, $[n\text{-}Bu_3B]_0$ = 0.05 mol/L, $[tratrate]_0$ = 1.0 mol/L.

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

b. Parameters of the first order Markovian statistics.

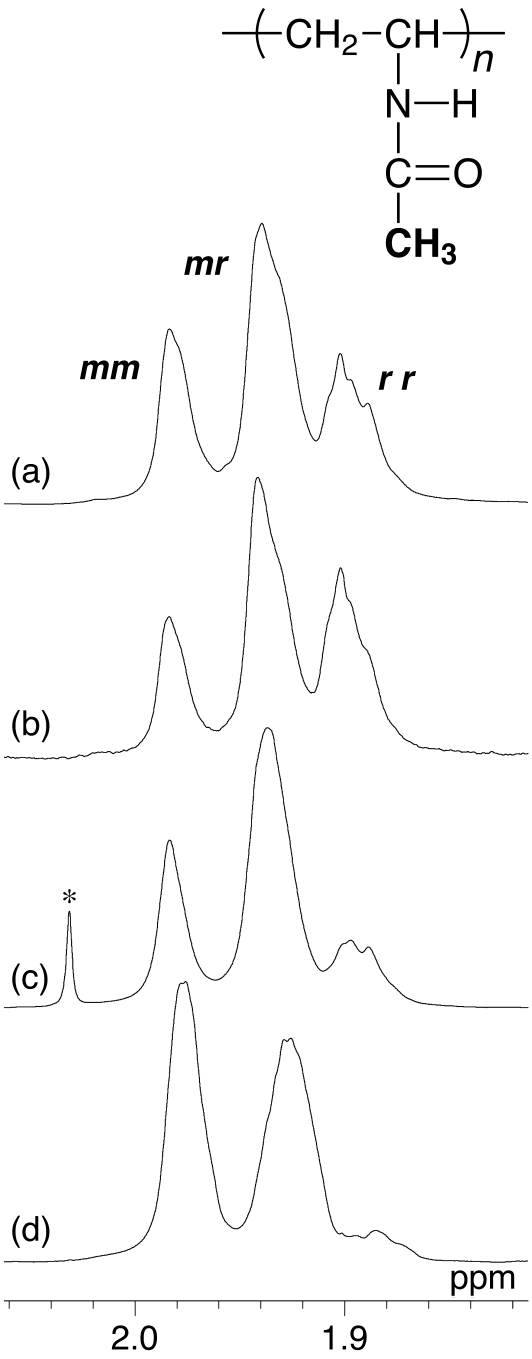


Fig. 1. Expanded ^{1}H NMR spectra of poly(NVA)s prepared (a) at 0°C without the added agents (Table 1, Run 1), (b) at –40°C in the presence of TBP (Table 1, Run 20), (c) at –40°C in the presence of HFIP (Table 2, Run 20), and (d) at –60°C in the presence of L-EtTar (Table 3, Run 4), as measured in D_2O at 25°C. (*: signal due to impurity)

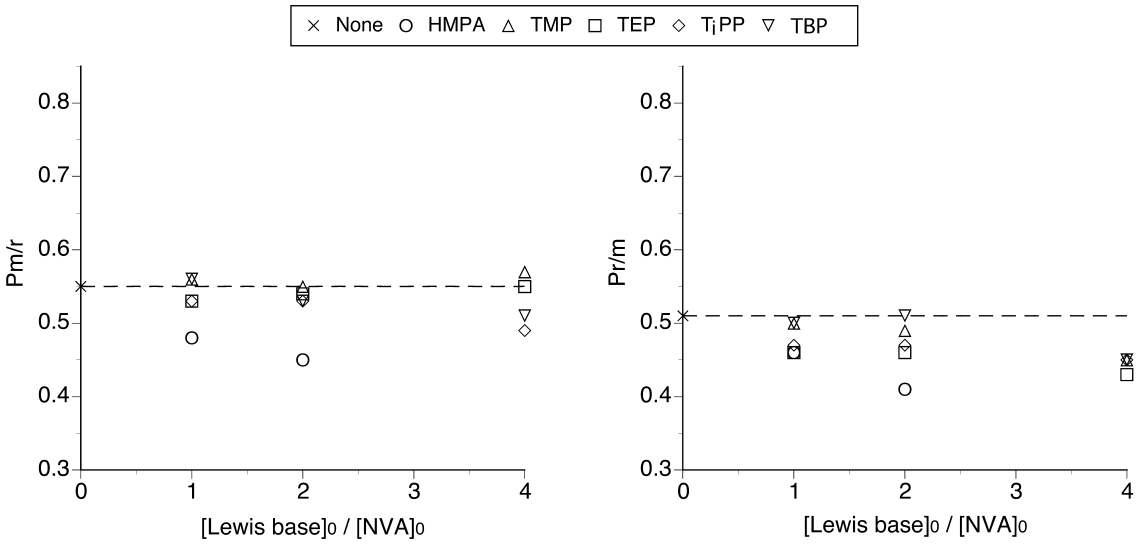


Fig. 2. Relationship between the parameters of the first order Markovian statistics and the $[\text{Lewis base}]_0$ / $[\text{NVA}]_0$ ratio for the NVA polymerization at 0°C in the presence of Lewis bases.

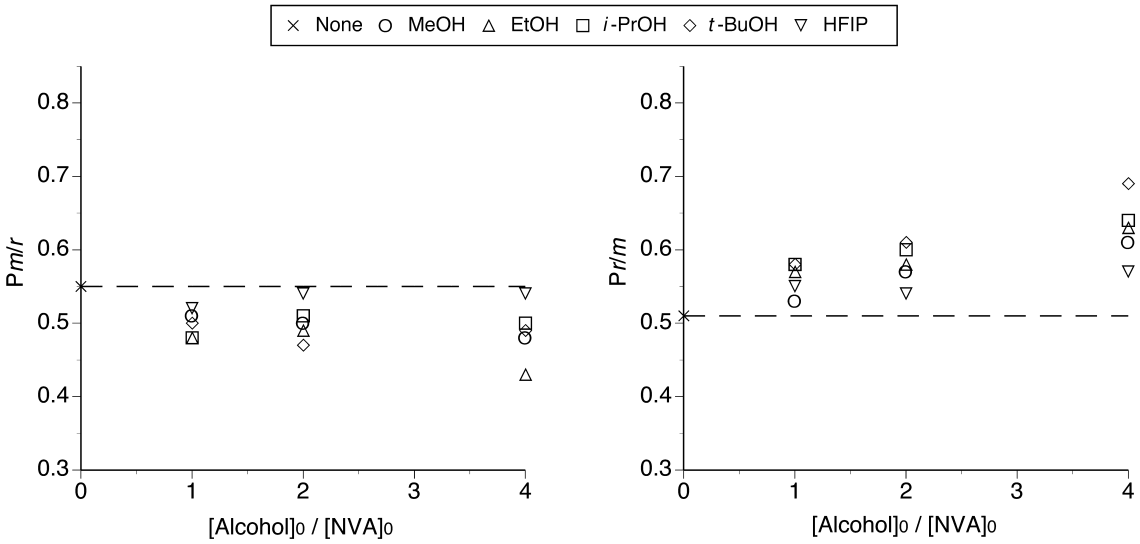


Fig. 3. Relationship between the parameters of the first order Markovian statistics and the $[Alcohol]_0$ / $[NVA]_0$ ratio for the NVA polymerization at 0°C in the presence of alcohols.

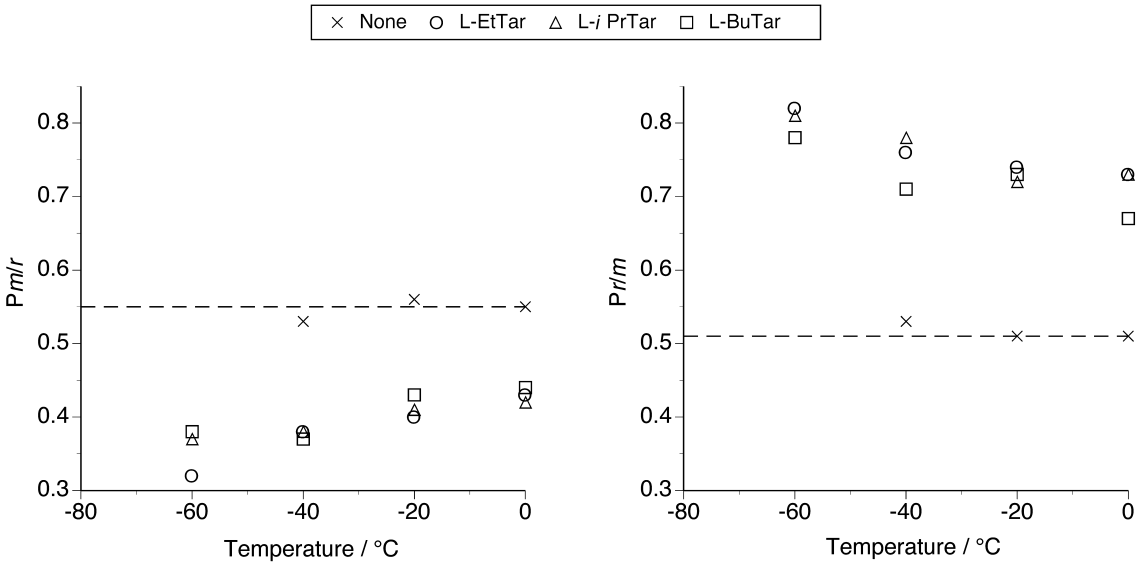


Fig. 4. Relationship between the parameters of the first order Markovian statistics and the polymerization temperature for the NVA polymerization in the presence of L-tartrates.

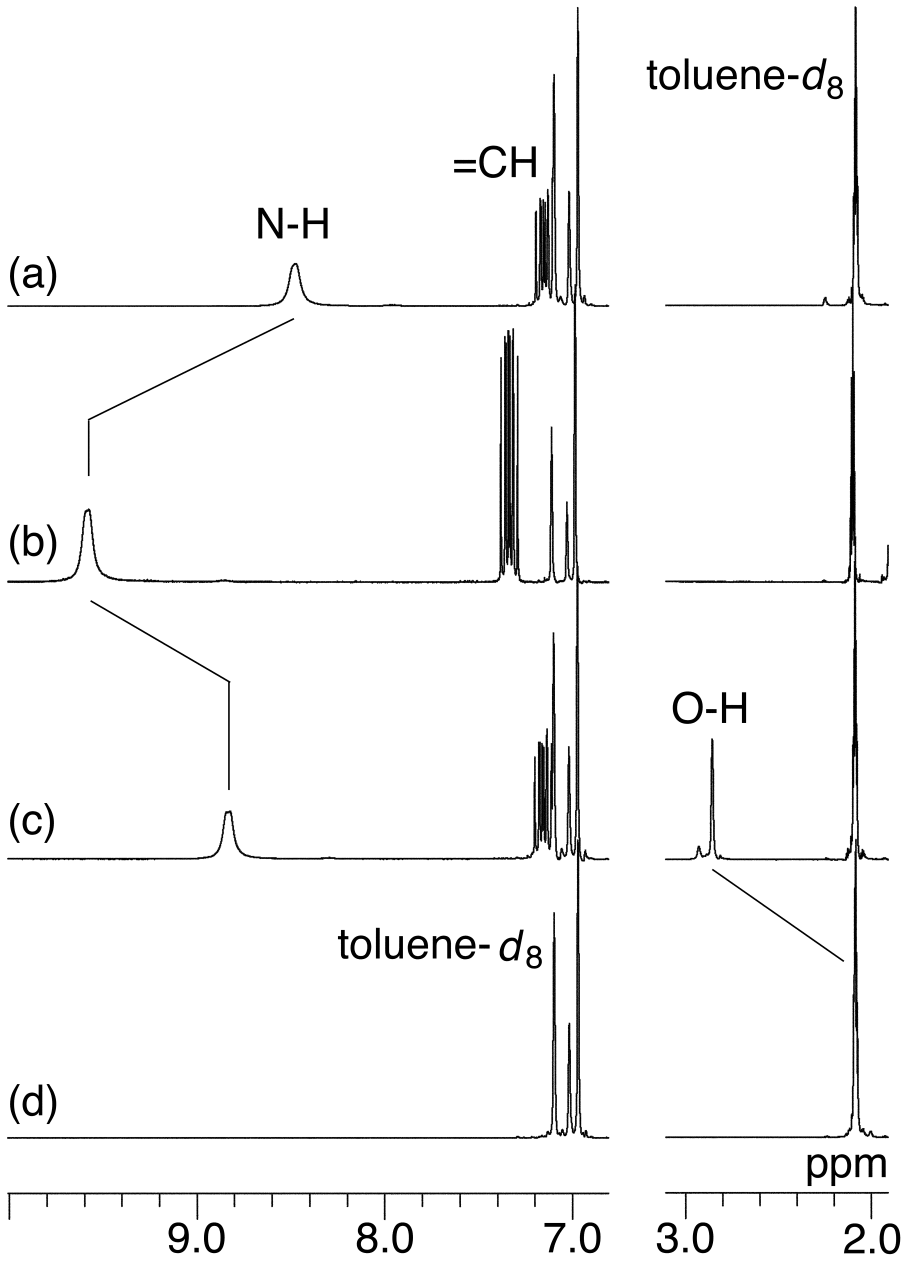


Fig. 5. Expanded ^{1}H NMR spectra of amide proton of NVA and/or hydroxyl proton of *t*-BuOH : (a) NVA, (b) equimolar mixture of NVA and TBP, (c) equimolar mixture of NVA and *t*-BuOH, and (d) *t*-BuOH, as measured in toluene-d_8 at 0°C.

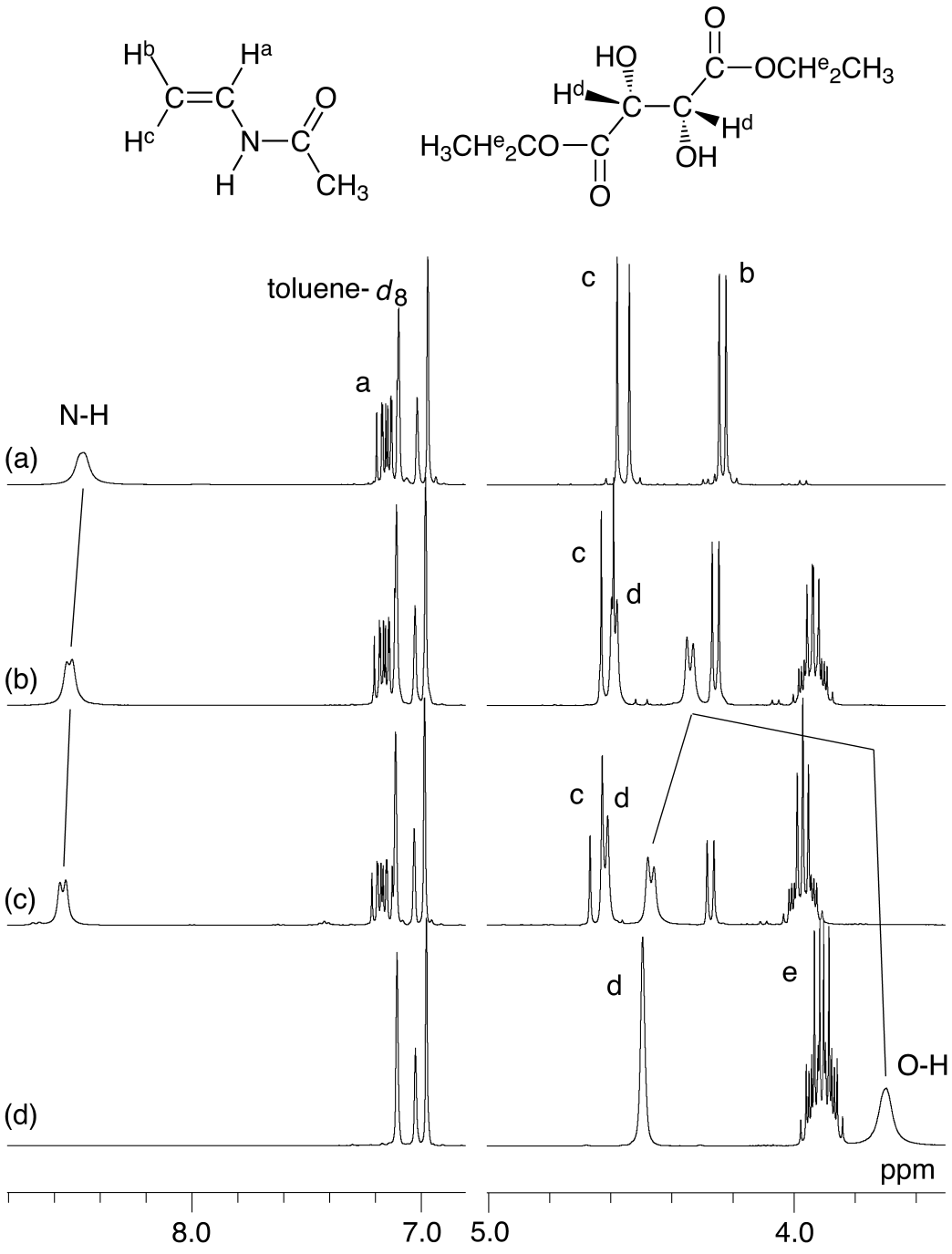


Fig. 6. Expanded ^{1}H NMR spectra of amide proton of NVA and/or hydroxyl proton of L-EtTar : (a) NVA (0.25 mol/L), (b) mixture of NVA (0.25 mol/L) and L-EtTar (0.125 mol/L), (c) equimolar mixture of NVA (0.25 mol/L) and L-EtTar (0.25 mol/L), and (d) L-EtTar (0.125 mol/L), as measured in toluene-d_8 at 0°C.

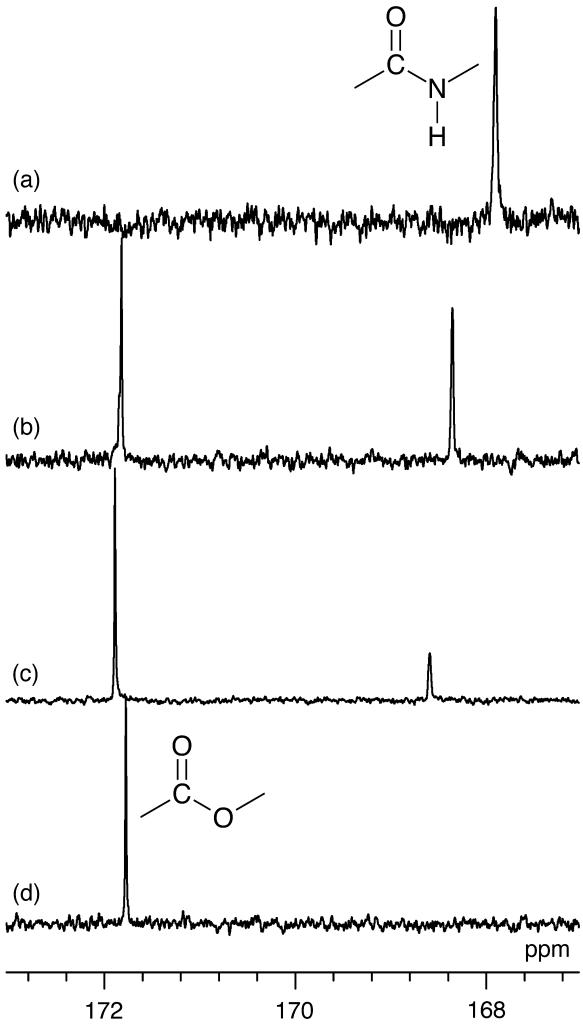


Fig. 7. Expanded ^{13}C NMR spectra of carbonyl carbons of NVA and/or L-EtTar : (a) NVA (0.25 mol/L), (b) mixture of NVA (0.25 mol/L) and L-EtTar (0.125 mol/L), (c) equimolar mixture of NVA (0.25 mol/L) and L-EtTar (0.25 mol/L), and (d) L-EtTar (0.125 mol/L), as measured in toluene-d_8 at 0°C.

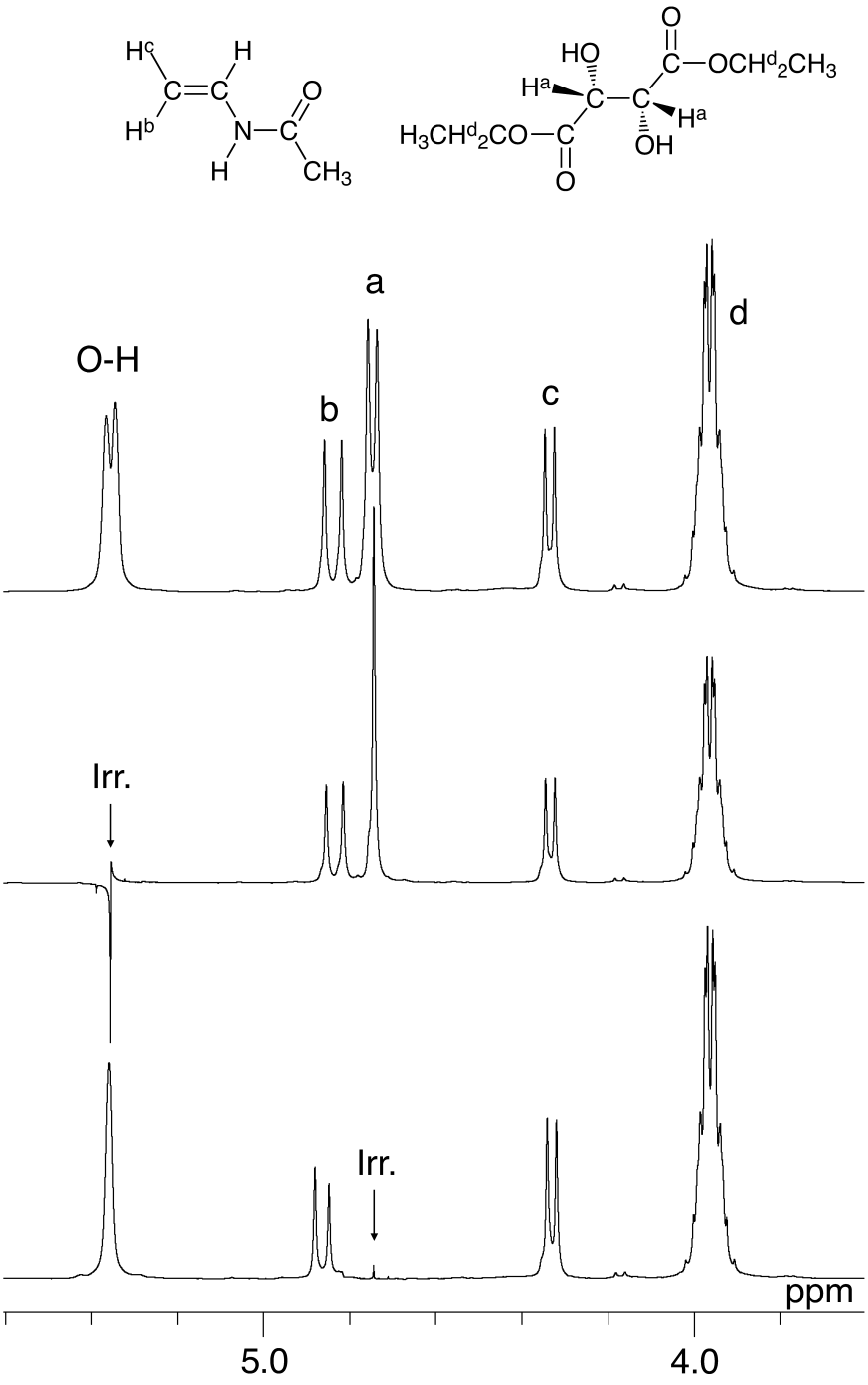
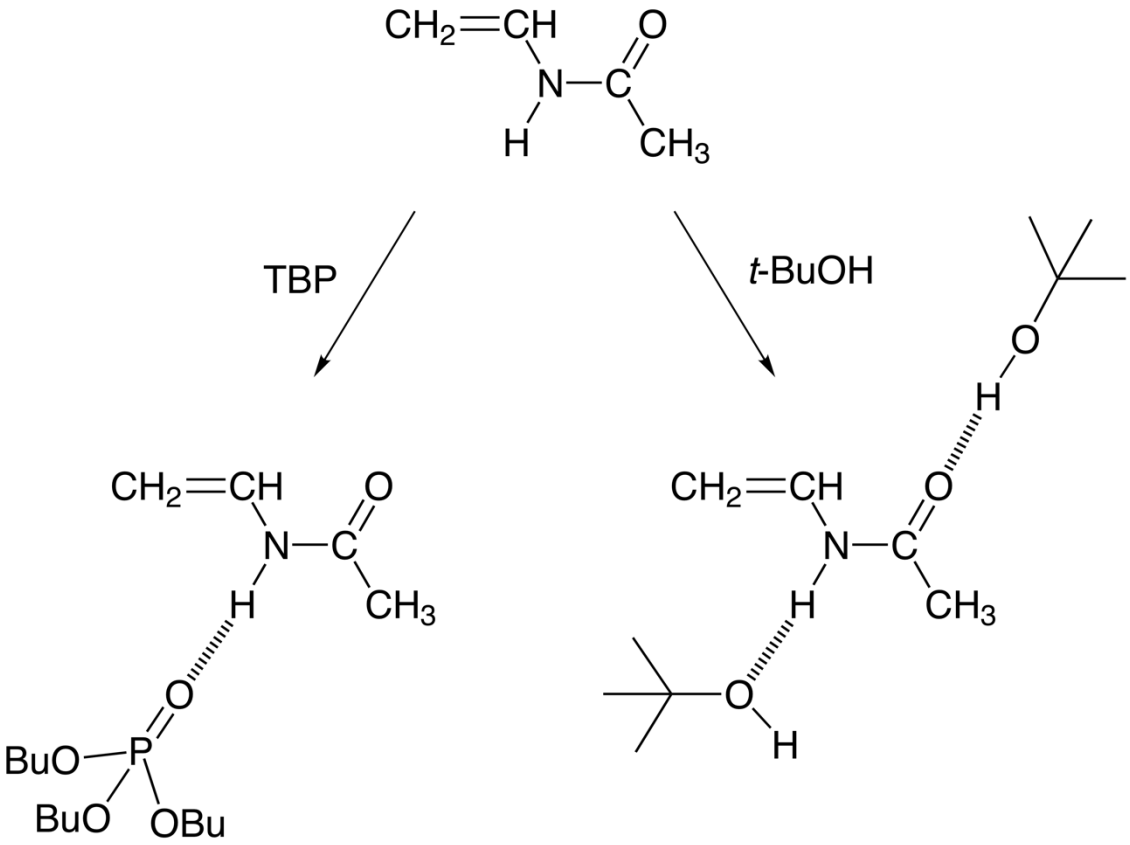
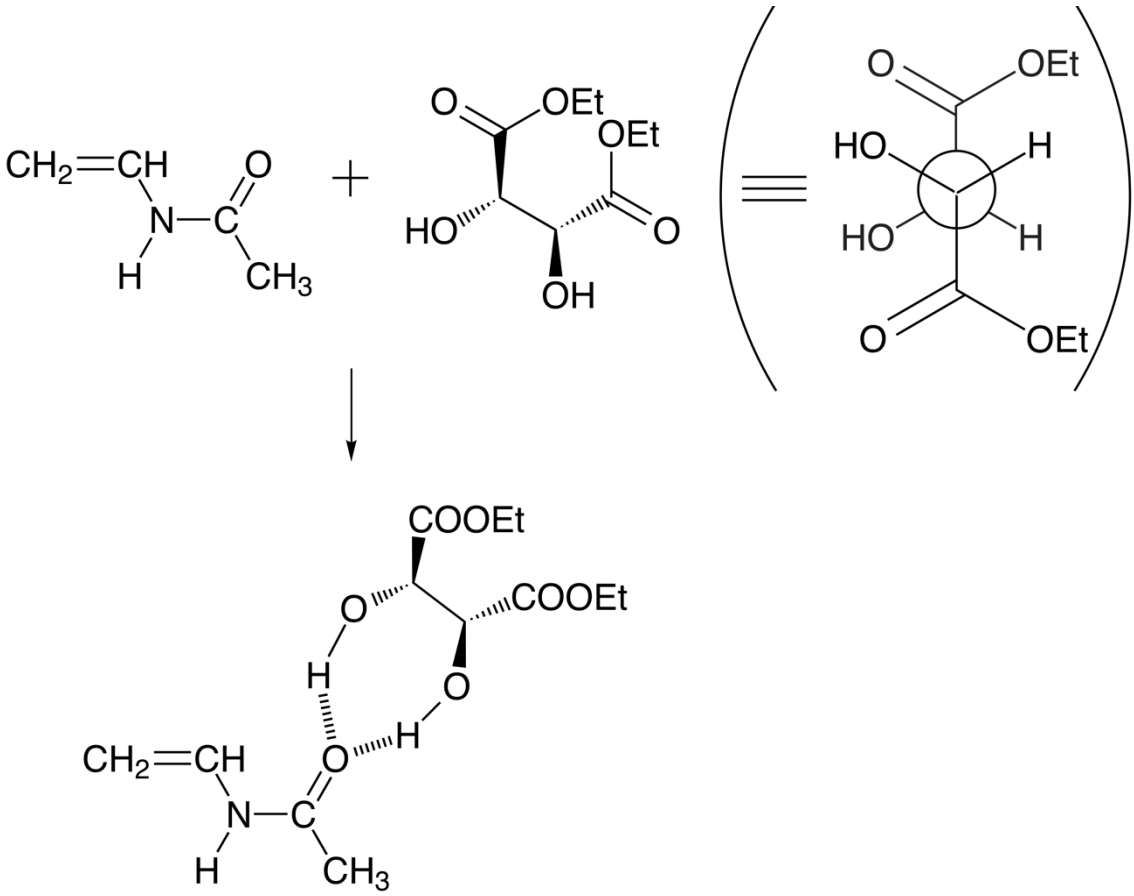


Fig. 8. Expanded ^{1}H NMR spectrum of (a) equimolar mixture of NVA (0.25 mol/L) and L-EtTar (0.25 mol/L), and spectra selectively spin-decoupled at the signal due to (b) hydroxyl protons and (c) methine protons, as measured in toluene-d_8 at –40°C.



Scheme 1. Possible structures of the hydrogen-bond-assisted complex of NVA with TBP or *t*-BuOH.



Scheme 2. Possible structure of the hydrogen-bond-assisted complex of NVA with L-EtTar.