

Stereochemistry of Radical Polymerization of Vinyl Esters in the Presence of Lewis Acid

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The synthesis of syndiotactic poly(vinyl alcohol) (PVA) is important because physical and chemical properties of PVA are greatly improved even by a slight increase in the main-chain syndiotacticity.¹ Because PVA is usually derived from poly(vinyl ester)s, it is necessary to control the stereochemistry of radical polymerization of vinyl esters to obtain stereoregular PVA. An efficient method of stereoregulation is based on solvent effect on radical polymerizations. Although solvent effect on the stereochemistry of vinyl acetate (VAc) polymerization is generally small,^{2–4} we have recently found pronounced solvent effects of fluoroalcohols on the polymerizations of VAc,^{5,6} vinyl pivalate (VPi),⁶ and vinyl benzoate (VBz),⁷ where a significant increase in syndiotacticity, heterotacticity, and isotacticity of the obtained polymers, respectively, was confirmed. The solvent effects are based on hydrogen-bonding interactions of fluoroalcohols with the side groups of the monomer and the growing chain end, which make the species apparently bulkier than their original size.

The present work investigates the radical polymerization of vinyl esters in the presence of Lewis acid (LA) compounds on the basis of the idea that the interaction between LA and side group (Lewis base) would also lead to the stereocontrol of vinyl ester polymerization. Many reports concerning the stereocontrol using LA have been published for the ionic polymerization including the anionic polymerization of (meth)acrylates and (meth)acrylamides⁸ and the cationic polymerization of vinyl ethers.⁹ In contrast, there are only a few reports on the stereochemical effects of LA in radical polymerization. Radical copolymerization of styrene and methyl methacrylate (MMA) in the presence of BCl₃ affords heterotactic copolymers.¹⁰

Homopolymerization of MMA in the presence of LA including SnCl₄, ZnCl₂, and MgBr₂ gave polymers with lower syndiotacticity compared with that obtained in the absence of the LAs.¹¹ However, there has been no report on the stereochemical effects of LA in the vinyl ester po-

lymerization to the best of our knowledge. This paper describes the stereochemical effects of the LAs on the radical polymerization of vinyl esters for the first time. The reaction systems investigated here include VAc and VPi as monomers and metal alkoxides such as aluminum tri-*t*-butoxide (Al(*Ot*Bu)₃) and methylaluminum bis(2,6-di-*t*-butyl-4-methylphenoxide) (MAD)¹² as LAs.

EXPERIMENTAL

Materials

VAc (Wako) and VPi (Wako) were purified by distillation. 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Tri-*n*-butyl borane ((*n*Bu)₃B) (Aldrich, 1.0 M solution in tetrahydrofuran) was used after removal of the solvent in vacuo. Aluminum triisopropoxide (Al(*Oi*Pr)₃) (Wako; purity > 99%), Al(*Ot*Bu)₃ (Aldrich; purity > 99%), MAD (TCI; 0.4 M solution in toluene), titanium tetraisopropoxide (Ti(*Oi*Pr)₄) (Wako; purity > 98%), zinc chloride (ZnCl₂) (Wako; purity > 99.9%) were used as obtained. The other reagents were purified by usual methods.

Polymerization Procedures

Polymerization was carried out under dry nitrogen in a dried glass tube equipped with a three-way stopcock. The reaction at 20°C was performed using AIBN under UV light irradiation (400-W high-pressure mercury lamp) or using (*n*Bu)₃B as reported.^{6,7} Monomer conversion was determined by ¹H NMR analysis of the reaction mixture in acetone-*d*₆ at room temperature. Reaction products of VAc polymerization were first precipitated into hexane, and then into aq. HCl (1N), filtered, dried, and saponified as reported.^{6,7} Poly(VPi) was recovered as a methanol-aq. HCl (1N) (1/1 v/v)-insoluble part. Saponification of poly(vinyl ester)s was performed as reported.^{6,7} The obtained PVA was collected by filtration, washed with methanol containing a small amount of acetic acid and with acetone, and dried under vacuum.

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Table I. Polymerization of VAc in the presence Lewis acid (LA) at 20°C^a

Run	Solvent	[VAc] ₀	LA	[LA] ₀	Appearance ^b	Time h	Yield ^c %	$\bar{M}_n \times 10^{-3}$ ^d	\bar{M}_w/\bar{M}_n ^d	Tacticity ^e			
										<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>r</i>
1	Benzene	2.0	None	0	Colorless, ○	48	35	5.6	1.6	20.7	48.4	30.9	55.1
2	Benzene	2.0	Ti(OiPr) ₄	0.50	Yellow gel	48	0	—	—	—	—	—	—
3	Benzene	2.0	Al(OiPr) ₃	0.50	Colorless, ×	48	16	5.0	1.6	18.7	48.9	32.3	56.8
4	Benzene	2.0	Al(OtBu) ₃	0.50	Yellow, ○	48	24	5.9	1.6	17.6	48.2	34.2	58.3
5	Benzene	2.0	Al(OtBu) ₃	1.0	Yellow, ○	48	43	6.1	1.6	17.3	46.8	35.9	59.3
6	Benzene	1.0	Al(OtBu) ₃	1.0	Orange, ○	96	11	6.1	1.4	19.1	48.5	32.4	56.6
7	Benzene	0.50	Al(OtBu) ₃	1.0	Yellow, ○	96	0	—	—	—	—	—	—
8	Benzene	2.0	MAD	0.50	Red, ○	48	16	6.0	1.4	18.8	47.9	33.2	57.2
9	Benzene	2.0	MAD	1.0	Red, ○	96	4	5.2	1.3	18.3	47.7	34.0	57.9
10	CH ₂ Cl ₂	2.0	None	0	Colorless, ○	24	54	5.8	1.7	21.9	50.1	28.0	53.0
11	CH ₂ Cl ₂	2.0	ZnCl ₂	0.50	Colorless, ×	24	73	4.8	1.8	20.4	49.2	30.4	55.0
12	CH ₂ Cl ₂	2.0	Al(OtBu) ₃	0.50	Pale yellow, ○	24	41	6.6	1.6	19.1	48.6	32.3	56.6
13	CH ₂ Cl ₂	1.0	Al(OtBu) ₃	1.0	Pale yellow, ○	48	15	5.3	1.5	20.1	49.0	30.9	55.4
14	CH ₂ Cl ₂	2.0	MAD	0.50	Red, ○	48	20	7.0	1.4	19.5	48.2	32.3	56.4

^a Polymerizations were initiated with (*n*Bu)₃B in the presence of a small amount of air. In a typical example, 10 mL of air were injected using a syringe to a reaction system consisting of 0.86 g (10 mmol) of monomer, 0.18 g (1 mmol) of (*n*Bu)₃B, and 4.1 mL of solvent. ^b Color and homogeneity of the polymerization system: ○, homogeneous; ×, heterogeneous. ^c Hexane- and aq.HCl-insoluble part. ^d Determined by SEC of original polymers using standard polystyrenes in THF. ^e Determined by ¹H NMR of PVA in DMSO-*d*₆.

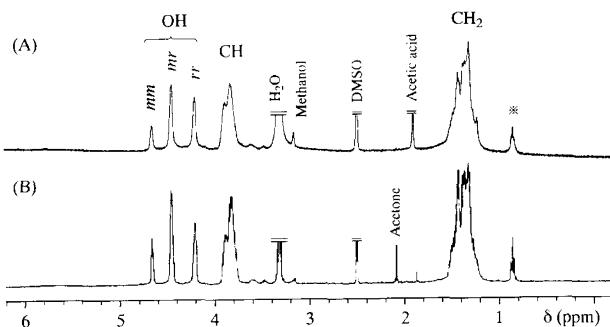


Figure 1. ¹H NMR spectra of PVA obtained through the polymerization of VAc at 20°C in the presence of Al(OtBu)₃ (A) (Table I, run 5) and in the absence of Al(OtBu)₃ (B) (Table I, run 1) (400 MHz, DMSO-*d*₆, r.t.). The asterisk peak is derived from the initiator fragment.

Measurements

The number-average molecular weight (\bar{M}_n) and polydispersity (\bar{M}_w/\bar{M}_n) of poly(vinyl ester)s were determined by size-exclusion chromatography (SEC) calibrated with standard polystyrenes using a Jasco PU-980 pump equipped with a Jasco RI-930 detector and TSK gel GMH_{HR}-H and G 3000 H_{HR} columns connected in series (eluent; THF, temperature; 40°C). Tacticity of PVA was determined from ¹H NMR spectra recorded on a Varian Gemini 2000 spectrometer (400 MHz) in dimethyl sulfoxide (DMSO)-*d*₆ at room temperature. The range of error in tacticity value is reported to be within ±0.5% for bulk polymerization of VAc based on the results of five repeated experiments (ref 6).

Titration Experiments

Hydrogen-bonding interactions between vinyl esters and LA were studied by titration. Stock solutions of a monomer and Al(OtBu)₃ in CDCl₃ were prepared (1.0 M) and portions of the two solutions were mixed in NMR tubes changing their ratio from 0 to 1. ¹³C NMR spectra were recorded on a Varian Gemini 2000 spectrometer (100 MHz) at 20 ± 1°C using tetramethylsilane (TMS) as

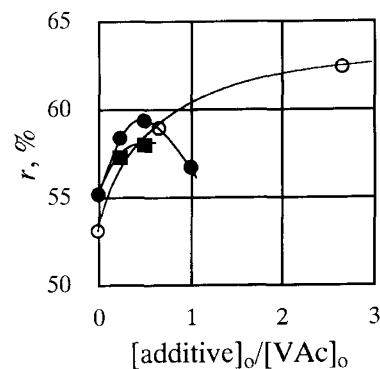


Figure 2. Relationship between [additive]₀/[VAc]₀ and syndiotacticity (*r*) of polymers obtained by the polymerization of VAc in the presence of LA at 20°C: additive = MAD (■), Al(OtBu)₃ (●), and (CF₃)₃COH (○). The results for the systems with (CF₃)₃COH are cited from ref 6. The polymerization using LA was carried out in benzene while that using (CF₃)₃COH in pure (CF₃)₃COH.

the internal standard.

RESULTS AND DISCUSSION

Polymerization of VAc in the Presence of Lewis Acid (LA)

Radical polymerization of VAc was carried out in the presence of various LAs (Table I). To avoid undesired reactions (for example, cationic oligomerization, hydrolysis, and deacetylation or dehydration),¹³ polymerization was carried out at 20°C. The cationic polymerization of VAc using ZnCl₂ in the absence of radical initiators at 20°C affords only a negligible amount of polymer.¹³ The polymerization of VAc in the presence of Ti(OiPr)₄ resulted in formation of a yellow gel (run 2). It is known that a yellow VAc-TiCl₄ complex is formed when VAc is mixed with TiCl₄.¹⁴ The mechanism of the gel formation observed in the present work may be due to the same reason. Decomposition of side chain or crosslinking involving cationic mechanism may also be responsible for the gelation. Polymerizations with the other LAs gave soluble polymers. ZnCl₂ had only negligible stereoeffect probably because of its low solubility in the polymeriza-

Table II. Polymerization of VPi in benzene in the presence of $\text{Al}(\text{O}t\text{Bu})_3$ at 20°C for 48 h^a

Run	[M] ₀	[Al(OtBu) ₃] ₀	Appearance ^b	Yield ^c		$\overline{M}_n \times 10^{-3}$ ^d	$\overline{M}_w/\overline{M}_n$ ^d	Tacticity ^e			
				%				mm	mr	rr	r
1	2.0	0	Colorless, ○	67		5.8	1.8	14.8	47.9	37.3	61.3
2	2.0	1.0	Pale yellow, ○	59		7.3	2.0	14.5	47.9	37.6	61.6
3	1.0	1.0	Pale yellow, ○	49		5.0	1.9	14.0	47.8	38.2	62.1

^a Polymerizations were initiated with $(n\text{Bu})_3\text{B}$ in the presence of a small amount of air. ^b Color and homogeneity of the polymerization system: ○; homogeneous, ×; heterogeneous. ^c MeOH/1N HCl(1/1)-insoluble part. ^d Determined by SEC of original polymers using standard polystyrenes in THF. ^e Determined by ¹H NMR of PVA in DMSO-*d*₆.

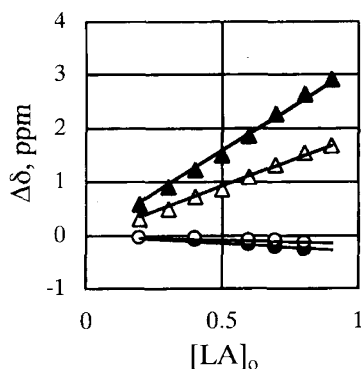


Figure 3. Changes in ¹³C NMR chemical shift of C=O (filled symbol) and H₂C (open symbol) of VAc in the presence of $\text{Al}(\text{O}t\text{Bu})_3$ (●, ○) or $(\text{CF}_3)_3\text{COH}$ (▲, △) [100 MHz, CDCl₃, $20 \pm 1^\circ\text{C}$, $[\text{VAc}]_0 + [\text{Al}(\text{O}t\text{Bu})_3]_0 = 1.0 \text{ M}$]. The results for the systems with $(\text{CF}_3)_3\text{COH}$ are cited from ref 15.

tion solvents (run 11). The polymerization system was heterogeneous throughout the reaction. Al compounds appeared to be effective in enhancing syndiotactic specificity of the VAc polymerization. Among the three Al complexes, $\text{Al}(\text{O}t\text{Bu})_3$ showed the largest syndiotacticity-enhancing effect. The effect of $\text{Al}(\text{O}t\text{Bu})_3$ was larger in benzene than in CH_2Cl_2 , suggesting that the stereochemical influence is based on polar interactions of the monomer and growing radical with the Al species. Figure 1 shows the ¹H NMR spectra of PVA obtained through the polymerization in the presence of $\text{Al}(\text{O}t\text{Bu})_3$ (A) and in the absence of $\text{Al}(\text{O}t\text{Bu})_3$ (B) (Table I, runs 5 and 1, respectively). The spectrum is evidence of the syndiotactic-rich structure of the polymer through the polymerization in the presence of $\text{Al}(\text{O}t\text{Bu})_3$ ($r = 59\%$). Figure 2 shows the relationship between $[\text{additive}]_0/[\text{VAc}]_0$ and diad syndiotacticity (r) of the polymers obtained by the VAc polymerization in the presence of additive or solvent including $\text{Al}(\text{O}t\text{Bu})_3$, MAD, and $(\text{CF}_3)_3\text{COH}$. In the range of $[\text{additive}]_0/[\text{VAc}]_0 = 0-0.5$, the syndiotacticity-enhancing effect of $\text{Al}(\text{O}t\text{Bu})_3$ and MAD was comparable to that of $(\text{CF}_3)_3\text{COH}$ which affords a polymer rich in syndiotacticity ($r \leq 72\%$).⁵ Although the reason why the effect of $\text{Al}(\text{O}t\text{Bu})_3$ at $[\text{additive}]_0/[\text{VAc}]_0 = 1$ was lower than that at $[\text{additive}]_0/[\text{VAc}]_0 = 0.25$ and 0.5 is not clear, this result shows that the complexation of both the monomer and the growing chain end may reduce the syndiotacticity-enhancing effect of the Lewis acid. Plots for $[\text{additive}]_0/[\text{VAc}]_0 = 0$ did not fall at the same positions probably because the polymerization solvents are different: the solvent for the VAc/LA systems is benzene at all $[\text{additive}]_0/[\text{VAc}]_0$ ra-

tios whereas the VAc/ $(\text{CF}_3)_3\text{COH}$ system at $[\text{additive}]_0 = 0$ is bulk polymerization.

Interaction between VAc and LA (NMR Titration)

LA is assumed to complex with the ester side groups of the monomer and growing chain-end, and make the side groups apparently bulkier as well as fluoroalcohols. To obtain information on the interaction between LA and ester group of VAc, ¹³C NMR titration experiment was carried out. Figure 3 shows changes in ¹³C NMR chemical shift of C=O and =CH₂ groups of VAc in the presence of $\text{Al}(\text{O}t\text{Bu})_3$ along with the results with $(\text{CF}_3)_3\text{COH}$.¹⁵ In contrast to the clear downfield shift observed with $(\text{CF}_3)_3\text{COH}$,¹⁵ no clear shift was confirmed with $\text{Al}(\text{O}t\text{Bu})_3$; although a yellow color appeared probably due to a complex formation. Although the interaction mode in the two systems should be different, this finding implies that the interaction between VAc and $\text{Al}(\text{O}t\text{Bu})_3$ may be much weaker than that between VAc and $(\text{CF}_3)_3\text{COH}$. This suggests two possible reasons for the observed stereoeffect: even a very weak VAc- $\text{Al}(\text{O}t\text{Bu})_3$ interaction may alter the polymerization stereochemistry or the Al species interact with the growing radical itself not with the side chain of the monomer and that of the growing chain. The latter possibility might be less plausible than the former because of the fact that the molecular weight and yield of the polymers were not clearly affected by the concentration of $\text{Al}(\text{O}t\text{Bu})_3$ (runs 1, 4, and 5 in Table I): a radical-Al interaction would be expected to decrease the reactivity of radical.

Polymerization of VPi in the Presence of LA

We examined the VPi polymerization in the presence of $\text{Al}(\text{O}t\text{Bu})_3$ (Table II). In contrast to VAc polymerization, the stereochemistry of VPi polymerization was little affected by $\text{Al}(\text{O}t\text{Bu})_3$, possibly due to weaker interaction between $\text{Al}(\text{O}t\text{Bu})_3$ and VPi than that between $\text{Al}(\text{O}t\text{Bu})_3$ and VAc. Steric repulsion between bulky VPi and bulky $\text{Al}(\text{O}t\text{Bu})_3$ may prevent effective interaction.

In conclusion, the stereochemical control of VAc polymerization was realized using Lewis acids ($\text{Al}(\text{O}t\text{Bu})_3$ or MAD) for the first time. A relatively weak Al-side chain interaction (Lewis acid-Lewis base interaction) may be responsible for the stereoeffect.

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REFERENCES AND NOTES

1. For reviews: a) C. A. Finch, Ed., "Polyvinyl Alcohol—Developments", Wiley, Chichester, 1992. b) K. Fujii, *J. Polym. Sci., Macromol. Rev.*, **5**, 431(1971). c) PVA no Sekai (The World of PVA) (in Japanese), Kobunshi Kankokai, Kyoto, 1992.
2. The polymerization in phenol has been reported to afford a polymer slightly rich in syndiotacticity ($r=56.5\%$): K. Imai, T. Shiomi, N. Oda, and H. Otsuka, *J. Polym. Sci., Part A: Polym. Chem.*, **24**, 3225 (1986).
3. T. Yamamoto, T. Yamamoto, T. Minamizawa, and M. Hirota, *Kobunshi Ronbunshu*, **36**, 557 (1979), *Chem. Abstr.*, **91**, 158200.
4. U. Kador and P. Mehnert, *Makromol. Chem.*, **144**, 29 (1971).
5. K. Yamada, T. Nakano, and Y. Okamoto, *Proc. Jpn. Acad.*, **74** (B), 46 (1998).
6. K. Yamada, T. Nakano, and Y. Okamoto, *Macromolecules*, **31**, 7598 (1998).
7. K. Yamada, T. Nakano, and Y. Okamoto, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 2677 (1999).
8. For a review: T. Nakano, and Y. Okamoto, in "Catalysis in Precision Polymerization", S. Kobayashi, Ed., Wiley, Chichester, 1997, pp 284—365.
9. For example: M. Sawamoto and M. Kamigaito, *Macromol. Symp.*, **107**, 43 (1996).
10. a) Y. Gotoh, T. Iihara, N. Kanai, N. Toshima, and H. Hirai, *Chem. Lett.*, 2157 (1990). b) Y. Gotoh, M. Yamashita, M. Nakamura, N. Toshima, and H. Hirai, *Chem. Lett.*, 53 (1991).
11. a) S. Okuzawa, H. Hirai, and S. Makishima, *J. Polym. Sci., Part A-1*, **7**, 1039 (1969). b) T. Otsu and B. Yamada, *Kogyo Kagaku Zasshi*, **72**, 359 (1969). c) A. Matsumoto and S. Nakamura, *J. Appl. Polym. Sci.*, **74**, 290 (1999).
12. MAD is a highly efficient LA catalyst for various organic reactions. For reviews, see: a) K. Maruoka and H. Yamamoto, in "Catalytic Asymmetric Synthesis", I. Ojima, Ed., Wiley, Chichester, 1993, pp 413—440. b) S. Saito and H. Yamamoto, *Chem. Commun.*, 1585 (1997).
13. a) A. F. Nikolayev, M. E. Rozenberg, V. A. Kuznetsova, T. V. Kreitser, and G. S. Popova, *Vysokomol. Soyed.*, **A 15**, 1440 (1973). b) M. Imoto, T. Otsu, and T. Ito, *Bull. Chem. Soc. Jpn.*, **36**, 310 (1963).
14. L. J. Carbonneau and R. W. Rees, *Chem. Ind.*, 656 (1958).
15. K. Yamada, T. Nakano, and Y. Okamoto, *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 220 (2000).