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Highly Isotactic Poly(vinyl alcohol). 2. Preparation and Characterization of Isotactic Poly(vinyl alcohol)

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ABSTRACT: The preparation and characterization of highly isotactic poly(vinyl alcohol)s (PVOHs) derived from poly(*tert*-butyl vinyl ether) (PtBVE) polymerized with $BF_3{\cdot}OEt_2$ were investigated. The mm sequence fraction increased with decreasing $BF_3{\cdot}OEt_2$ concentration, and it reached as high as 78−79%, which seems to be the highest value of all so-called isotactic PVOHs reported so far, but only if the catalyst concentration was reduced to below 0.5×10^{-3} mol/L. An increase in mm sequence fraction may be caused by highly isospecific propagation of a new kind of species, which is thought to be generated from ligand exchange of the BF_3 complex from ether to water. We also studied the polymerization of tBVE with various BF_3 complexes, such as $BF_3{\cdot}2CH_3COOH$, $BF_3{\cdot}2CH_3OH$, or $BF_3{\cdot}2CH_3OH$. The mm sequence fraction increased in the following order: $BF_3{\cdot}2CH_3COOH < BF_3{\cdot}OEt_2 < BF_3{\cdot}2MeOH < BF_3{\cdot}2H_2O$. It increased with a reduction in the catalyst concentration for each type of catalyst.

Introduction

Many investigations have been reported on the synthesis of stereoregular poly(vinyl alcohol)s (PVOHs)—syndiotactic PVOH and isotactic PVOH. Although they are just a little rich in the syndiotactic or the isotactic sequence, a marked dependence of stereoregularity on their properties has been recognized, which may be caused by changing intra- and intermolecular hydrogen bonding.[1,2]

A series of vinyl ester have been polymerized by free radical polymerization to convert to stereoregular PVOHs with a rich syndiotactic or isotactic sequence. The physical and solution properties of the PVOHs were also studied in relation to their stereoregularity.[1,2] The stereoregularity of the PVOH derived from poly(vinyl acetate) (PVAc), which is available commercially, is approximately atactic. Vinyl pivalate[3] and vinyl trifluoroacetate[4] yield a small amount of syndiotactic-rich PVOHs compared to commercially available PVOH, meanwhile vinyl benzoate and its derivatives yield a small amount of isotactic-rich PVOHs.[5]

Vinyl ethers such as benzyl vinyl ether (BzVE), *tert*-butyl vinyl ether (tBVE), and trimethylsilyl vinyl ether (VOSi) have been also studied as starting monomers to obtain stereoregular PVOHs. Murahashi et al. successfully prepared the isotactic-rich PVOH by cationic polymerization of BzVE followed by hydrolysis with hydrogen bromide.[6] Yuki et al. studied closely the relationship between the polymerization conditions of BzVE and the polymer tacticity by analyzing the ^1H NMR spectrum of methylene proton at the side chain of polyBzVE (PBzVE).[7] The fraction of mm sequence increased with decreasing polymerization temperature and reducing monomer concentration, and it was also influenced by the polarity of the polymerization medium. In an attempt to attain higher stereoregularity and easier conversion to PVOH, tBVE was investigated by Okamura et al.[8] They studied in detail the relationship between the polymerization conditions of tBVE and the polymer tacticity, and isotactic-rich PVOH was produced by polymerization with boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$) in nonpolar media. Murahashi et al. prepared PVOHs with wider range of tacticity

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Table 1. Characterization of Isotactic PVOHs Derived from PtBVE Prepared with $BF_3{\cdot}OEt_2$ in Toluene at −78 °C

					PtBVE			PVOH			
								triad (%)			
no.	[tBVE] (vol %)	$[BF_3{\cdot}OEt_2]$ (mM)	time (h)	conv (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	mm	mr	rr	$\bar{P}_{rac}$
1	5	1.25	3	73.1	59 000	121 200	2.05	67.1	26.9	6.0	1400
2	5	0.50	2	80.9	58 290	120 720	2.07	79.2	18.4	2.4	1370
3	5	0.25	4	85.2	212 900	507 820	2.39	78.8	18.9	2.3	6800
4	10	0.25	10	78.7	32 030	60 680	1.89	78.4	18.8	2.8	490
5[a]								55	32	13[b]	
								(79	17	4)[c]	
6[d]								70.2	22.5	7.3[e]	
								(86	10	4)[c]	

[a] Isotactic PVOH derived from PtBVE reported by Okamura et al.[8] [b] Triad sequence fractions determined by ^{1}H NMR spectrum on PVOH.[13] [c] Triad sequence fractions determined by ^{1}H NMR spectrum on PVAc.[9] [d] Isotactic PVOH derived from PVOSi prepared by Murahashi et al.[9] [e] Triad sequence fractions determined by ^{1}H NMR spectrum on PVOH.[10]

using VOSi whose polymer could be converted to PVOH immediately by being just barely dissolved in methanol.[9] On one hand, isotactic-rich PVOH was obtained by cationic polymerization of VOSi with ethyl aluminum dichloride ($EtAlCl_2$) in toluene; on the other hand, syndiotactic-rich PVOH was obtained with stannic chloride in nitroethane.

A lot of effort has been made to prepare stereoregular PVOHs as mentioned above; the stereoregularity, however, has remained at a low level: mm = 70% at best for so-called isotactic PVOH derived from polyVOSi (PVOSi).[9,10]

We previously reported the PVOH having the highest isotactic sequence of all isotactic PVOHs reported so far.[11] This PVOH showed some interesting physical properties different from the previously reported isotactic PVOH as well as the commercial atactic PVOH, which will be reported elsewhere. In the present paper, details of the preparation and the characterization of this highly isotactic PVOH were dealt with.

Experimental Section

Reagents. *tert*-Butyl vinyl ether (tBVE) monomer was prepared by alkyl exchange reaction between *tert*-butyl alcohol and lauryl vinyl ether in the presence of $Hg(OAc)_2$. To eliminate traces of alcohols, the monomer was washed with water, dehydrated over potassium hydroxide, and distilled over calcium hydride before use: bp 78 °C (lit. 76.5−78 °C). The purity was further confirmed by gas chromatography. Solvents were purified and dehydrated carefully by the usual methods. Boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$) was purified by distillation under reduced nitrogen pressure and used as a toluene or methylene chloride solution. Other boron trifluoride complexes were used as toluene solutions without further purification.

Polymerization. The polymerization of tBVE was carried out with boron trifluoride complexes in several solvents such as toluene or methylene chloride at various temperatures. An ampule equipped with a three-way stopcock was flushed with dry nitrogen, and then the solvent and the catalyst were introduced with a syringe. To this catalyst solution cooled at a given temperature was slowly added the monomer solution with a syringe, and the ampule was sealed off immediately. Adding a small amount of methanol that was cooled to the same temperature as the reaction mixture terminated the polymerization. The mixture was then poured into a large amount of methanol, and the precipitated polymer was washed with methanol and dried under vacuum.

Preparation of PVOH from PolytBVE (PtBVE). PtBVE was converted into PVOH with hydrogen bromide (HBr) gas at 0 °C. Before dry HBr gas was passed slowly through a 1−5 wt % solution of PtBVE in methylene chloride or toluene with stirring, dry nitrogen being passed to remove oxygen dissolved in the solution. After 5−10 min blowing of HBr gas, a white precipitate appeared. The reaction mixture was then poured into a large amount of ammoniacal methanol and the precipitate was collected by filtration, washed with methanol, and dried under vacuum.

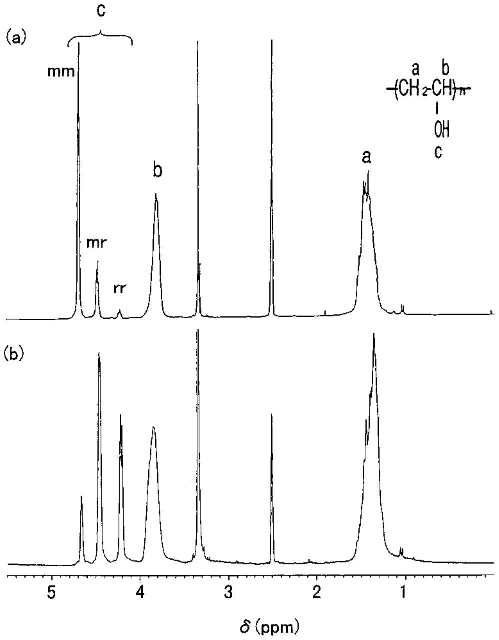


Figure 1. ^{1}H NMR spectra of stereoregular PVOHs in DMSO-d_6, at 25 °C and 270 MHz: (a) highly isotactic (run 2 in Table 1); (b) moderately syndiotactic (run 2 in Table 3). mm, mr, and rr are assigned to meso−meso, meso−racemic, and racemic−racemic sequence fractions, respectively.

Acetylation of PVOH. A 1 g sample of PVOH powder was suspended in 10 mL of dry pyridine at room temperature. After the PVOH was swollen, 5 mL of acetic anhydride was added. Then the reaction mixture was heated at 100 °C with shaking at intervals, and heated for another 1 h after the PVOH was dissolved absolutely. After reaction, the mixture was poured into 500 mL of water, and the precipitated polymer was collected by filtration. The PVAc thus obtained was purified by precipitation from acetone with water and then dried under vacuum.

Molecular Weight Measurement. Molecular weight and its distribution of PtBVE were measured by GPC at 38 °C in THF as an eluent with Shimazu Model 802A hichromatograph equipped with a differential refractometer detector. The molecular weight calibration was obtained by using standard polystyrenes. The degrees of polymerization of PVAc ($\bar{P}_{rac}$) were measured by same method described in previous paper.[11]

NMR Measurement. ^{1}H NMR measurements were performed on a JEOL type GSX-270 spectrometer operating at 270.17 MHz. The spectra of PVOH were measured in diethyl-d_6 sulfoxide (DMSO-d_6) at 25.0 °C.

Stereoregularity Determination. The triad sequence fractions of PVOH can be determined by ^{1}H NMR spectrum

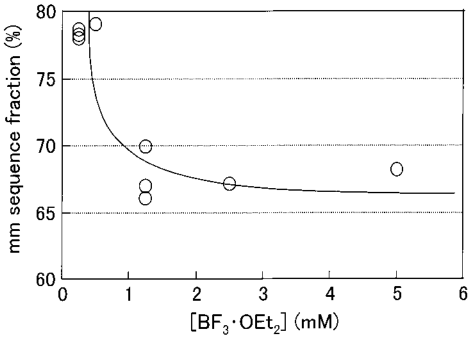


Figure 2. Effect of catalyst concentration on the mm sequence fraction of PVOHs derived from PtBVE prepared with BF_3·OEt_2 in toluene at −78 °C.

Table 2. Characterization of Isotactic PVOHs Derived from PtBVE Prepared at Various Monomer Concentrations with BF_3·OEt_2 in Toluene at −78 °C

				PtBVE			PVOH triad (%)		
no.	[tBVE] (vol %)	time (h)	conv (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	mm	mr	rr
1	50	3	21.5	101 500	221 800	2.19	64.5	29.5	6.0
2	25	3	34.8	91 700	167 500	1.83	72.0	24.2	3.8
3	10	7.5	61.6	30 400	52 100	1.71	76.1	20.9	2.9
4	5	3	80.6	81 300	140 600	1.73	77.0	20.0	3.0
5	2.5	19	51.3	47 500	85 500	1.80	77.0	20.1	2.9

measured in DMSO-d_6.[12] Figure 1 illustrates the ^1H NMR spectra of several stereoregular PVOHs derived from PtBVEs.

Results and Discussion

Preparation of Highly Isotactic PVOH. The polymerization of tBVE was carried out with various BF_3·OEt_2 concentrations in toluene at −78 °C, and then the resultant PtBVEs were converted into the PVOHs. The results are summarized in Table 1 and mm sequence fraction of the PVOHs is shown in Figure 2 as a function of BF_3·OEt_2 concentration. The mm sequence fraction increased with decreasing BF_3·OEt_2 concentration and it reached as high as 78−79% when the BF_3·OEt_2 concentration was reduced below 0.5×10^{-3} mol/L.

Because the stereoregularity of PVOH can be determined by several spectroscopic methods,[1,12,13] it should be noted how we measured the stereoregularity of the polymers. The observation of the methyl proton signal of PVAc by ^1H NMR spectrum was the most popular method to determine the stereoregularity of PVOH because PVOH is easily converted to PVAc with retention of its stereoregularity. However, the tacticity determination therefrom seems difficult because of the close chemical shifts and broad rr absorption peak.[1,14] The relative peak height analysis may overestimate the mm sequence fraction. On the other hand, Moritani et al.[12] and DeMember et al.[13] found that the hydroxyl proton absorption splits into three separate peaks due to the triad tacticity in ^1H NMR spectrum of PVOH in DMSO-d_6. These three peaks are sharp and separate enough from each other to determine the stereoregularity as shown in Figure 1. It is believed that ^1H NMR measurement of PVOH in DMSO-d_6 can give a more accurate tacticity than that of the corresponding PVAc. For the purpose of comparison, Table 1 includes mm sequence fraction values determined by ^1H NMR spectra on PVAc and PVOH of some typical isotactic PVOHs ever reported. The value of the PVOH derived from PtBVE, which is obtained by a process proposed by Okamura et al.,[8] is 79% determined on PVAc and 55% on PVOH,[13] and the value of the PVOH derived from PVOSi, which is prepared by Murahashi et al.,[9] is 86% on PVAc and 70.2% on PVOH.[10] This fact indicates the mm sequence fraction value determined on PVAc is much larger than that determined on PVOH and suggests that the mm sequence fraction of the isotactic PVOH derived from PBzVE, whose mm sequence fraction is 89% determined on PVAc, as reported by Yuki et al.,[7] may likewise be similar to that of the PVOH prepared by Murahashi et al. It has also been reported that a PVOH derived from PtBVE prepared with BF_3·OEt_2 in toluene at −78 °C has a mm sequence fraction of 49.7% as determined on PVOH.[12] At all events, the PVOH prepared in this work seems to be the most highly isotactic PVOH ever reported. Figure 1a shows the ^1H NMR spectrum of highly isotactic PVA (run 2 in Table 1) derived from PtBVE which is prepared with BF_3·OEt_2 at very low catalyst concentration.

To clarify the reason these highly isotactic PVOHs (PtBVEs) were obtained by using the identical catalyst as previously reported experiments, we studied closely the polymerization conditions.

Effect of Monomer Concentration. The effect of tBVE monomer concentration on the polymerization carried out with BF_3·OEt_2 of 0.25×10^{-3} mol/L in toluene at −78 °C is summarized in Table 2. The mm sequence fraction of the PVOH (PtBVE) increased from 64.5% to 77% with decreasing initial tBVE concentration from 50 vol % to 2.5 vol %. Our results seem to agree with Okamura's finding that the dielectric constant of the polymerization system affects stereoregularity of the produced polymer.[8] It is apparent by comparison with Tables 1 and 2 that reducing the tBVE monomer concentration is not as effective as reducing catalyst concentration to raise the mm sequence fraction of the produced polymer.

Polymerization in Various Solvents. The results of the polymerization carried out in various solvents and characterizations of resultant PVOHs are summarized in Table 3. Using a polar solvent such as methylene

Table 3. Characterization of Stereoregular PVOHs Derived from PtBVE Prepared with BF_3·OEt_2 at −78 °C in Various Solvents

						PtBVE			PVOH triad (%)		
no.	solv	[tBVE] (vol%)	[BF_3·OEt_2] (mM)	time (h)	conv (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	mm	mr	rr
1	CH_2Cl_2	10	2.50	60	70.0	26 000	56 900	2.19	19.1	48.9	32.0
2	CH_2Cl_2	10	0.25	60	70.0	52 100	99 300	1.91	11.2	54.0	34.8
3	$EtNO_2$	10	2.50	3	67.2	1 640	5 000	3.05	18.7	55.0	26.3
4	$EtNO_2$	10	0.25	3	2.8	26 800	38 100	1.42	16.3	53.1	30.6
5	hexane	10	2.50	3	89.1	74 300	360 300	4.85	50.6	38.2	11.2
6	hexane	10	0.25	3	8.9	103 500	284 500	2.75	49.6	37.0	13.4
7	heptane	5	2.50	3	92.5	136 000	966 000	7.10	54.1	35.8	10.1
8	heptane	5	0.25	3	75.5	187 000	642 000	3.43	53.8	35.3	10.9
9	MCH	5	2.50	6	99.0	110 000	281 000	2.55	50.3	39.3	10.4
10	MCH	5	0.50	6	89.0	33 700	111 000	3.29	52.5	36.9	10.6

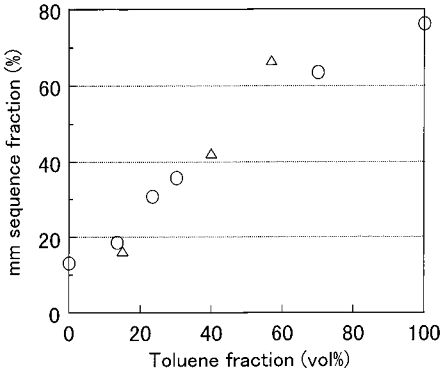


Figure 3. Effect of the polarity of solvent on the mm sequence fraction of PVOHs derived from PtBVE prepared with $BF_3 \cdot OEt_2$ in toluene−methylene chloride mixture at −78 °C. Initial concentrations of tBVE were 10 (○) and 5 (△) vol %.

chloride (CH_2Cl_2) or nitroethane ($EtNO_2$), the rr sequence fraction increased, while the mm sequence fraction increased in a nonpolar solvent such as *n*-hexane, *n*-heptane, or methylcyclohexane (MCH).

In CH_2Cl_2, the polymerization proceeded homogeneously as is the case with in toluene, but the polymerization rate was slower and the molecular weight of the obtained PtBVE was lower compared to that obtained in toluene. The polymerization in $EtNO_2$, however, proceeded heterogeneously due to low solubility of PtBVE in $EtNO_2$ and therefore the rr sequence fraction of the resultant PVOH was lower than that obtained in CH_2Cl_2.

The stereoregularity of PVOHs (PtBVEs) polymerized in toluene/CH_2Cl_2 mixtures are shown in Figure 3 as a function of mole fraction of toluene, indicating that the mm sequence fraction increased monotonically with increasing toluene fraction. These results may be interpreted according to the consideration proposed by Okamura et al.[8] that the isotactic propagation preferred homogeneous and nonpolar conditions at low temperature. The mm sequence fraction of PVOHs (PtBVEs) obtained in toluene, however, was much higher than that obtained in *n*-hexane, *n*-heptane, or methylcyclohexane, whose mm sequence fractions were mutually almost the same despite their different dielectric constants and solubility parameters. This fact may suggest that, in the case of toluene, some kind of interaction between the propagation site and electron of toluene should be allowed as a factor which influences the stereospecific propagation. It is well-known that aromatic groups of solvent, additive, monomer, or polymer interact with the growing chain in carbocationic polymerization.[15] Therefore the local polarity around the propagation site in toluene may be lower than the average polarity of the polymerization mixture due to the selective solvation of toluene to the carbenium ion caused by electron interaction which would promote isospecific propagation. In contrast, the local polarity in aliphatic solvents such as methylcyclohexane may be higher than the average polarity because of the selective solvation of tBVE to the carbenium ion. Thus, we concluded that toluene is one of the best solvents possible to obtain the highly isotactic polymer in polymerization of tBVE with $BF_3 \cdot OEt_2$.

Table 4. Characterization of Isotactic PVOHs Derived from PtBVE Prepared with $BF_3 \cdot OEt_2$ of 0.25×10^{-3} mol/L in Toluene at Various Temperatures

				PtBVE			PVOH			
							triad (%)			
no.	temp (°C)	time (h)	conv (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	mm	mr	mr	$\bar{P}_{rac}$
1	0	3	~0	2 380	3 620	1.52				
2	−20	3	57.5	26 500	40 200	1.52	64.5	29.5	6.0	
3	−40	3	37.5	41 000	87 600	2.14	72.0	24.2	3.8	1070
4	−60	3	62.5	70 100	142 500	2.03	76.1	20.9	2.9	2020
5	−78	3	25.1	74 200	150 000	2.02	79.1	18.9	2.0	3540

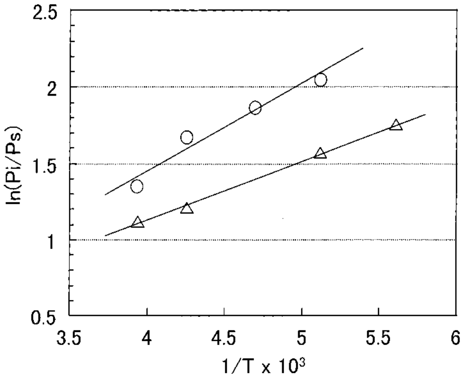


Figure 4. Temperature dependence on stereoregularity of isotactic PVOHs derived from PtBVE prepared with $BF_3 \cdot OEt_2$ in toluene. Catalyst concentrations were 0.25 mmol/L (○), and 2.5 mmol/L (△).

Table 5. Activation Parameters in Isotactic and Syndiotactic Propagation of Isotactic PVOHs

concn of catalyst	$\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ (cal/mol)	$\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ (cal/deg mol)
low (0.25 mM)	−1140	−1.70
high (2.50 mM)	−770	−0.85

Effect of Polymerization Temperature. We next examined the effect of temperature on the polymerization of tBVE. Table 4 indicates the results of the polymerization conducted in toluene with $BF_3 \cdot OEt_2$ of 0.25×10^{-3} mol/L at various temperatures between −78 and 0 °C. Except for the polymerization at 0 °C, a high molecular weight and a high mm sequence fraction of the PtBVEs (PVOHs) were obtained and both of them increased with decreasing polymerization temperature. This result means that dropping the polymerization temperature to the lowest possible extent is really effective to obtain high molecular weight and highly isotactic PVOHs(PtBVEs).

Nozakura et al.[16] have reported that the mechanism of stereoregulation could be inferred from Fordham's equation (eq 1).[17] Here, P_i, and P_s denote the mole fractions of meso and racemic, respectively; R is the gas constant, and T is the absolute temperature. Analyzing

$$\ln(P_i/P_s) = (\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger})/R - (\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger})/RT \quad (1)$$

the stereoregularity of the resultant polymers according to eq 1, we can obtain some information about the regulation of the polymerization. Is monomer addition governed enthalpically or entropically? In Figure 4, the relationships between reciprocal temperature ($1/T$) and logarithm of the meso/racemic ratio ($\ln(P_i/P_s)$) for two $BF_3 \cdot OEt_2$ concentration levels of 0.25×10^{-3} and 2.5×10^{-3} mol/L are plotted, and the activation parameters calculated therefrom are listed in Table 5. Both activation enthalpy and activation entropy of the isotactic propagation are smaller than those of the syndiotactic propagation and their differences are 1140 cal/mol and 1.7 cal/(deg mol) for 0.25×10^{-3} mol/L, and 770 cal/mol and 0.85 cal/(deg mol) for 2.5×10^{-3} mol/L, respectively. This indicates that the isotactic propagation was pre-

Table 6. Characterization of Isotactic PVOHs Derived from PtBVE Prepared with $BF_3 \cdot OEt_2$ in the Presence of Various Amounts of Water in Toluene at − 78 °C

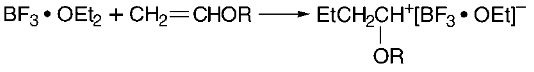
no.	$[BF_3 \cdot OEt_2]$ (mM)	$[H_2O]$ (mM)	time (h)	conv (%)	PtBVE $\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	PVOH triad (%) mm	mr	rr
1	5.00	1.00	3	94.6	94 500	307 000	3.25	68.3	26.7	5.0
2	2.50	1.12	4	76.6	33 930	72 240	2.13	67.3	26.6	6.1
3	1.25	0.96	2	71.5	116 900	258 300	2.21	66.1	28.3	5.7
4	1.25	9.38	5	60.6	27 300	47 300	1.73	74.1	22.1	3.8
5	1.25	22.1	12	70.6	24 400	40 700	1.67	74.8	21.3	3.9
6	0.25	0.96	3	71.2	115 600	291 500	2.52	78.4	19.2	2.4
7	0.25	9.38	16	60.0	23 300	39 600	1.70	78.5	18.9	2.6
8	0.25	22.1	36	0						

Table 7. Characterization of Isotactic PVOHs Derived from PtBVE Prepared with various BF_3 Complexes in Toluene at −78 °C

no.	catalyst	[cat] (mM)	time (h)	conv (%)	PtBVE $\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	PVOH triad (%) mm	mr	rr
1	$BF_3 \cdot 2H_2O$	10.0	3.5	82.2	81 300	170 500	2.10	72.8	23.9	3.3
2	$BF_3 \cdot 2H_2O$	5.00	3.5	62.2	55 100	105 400	1.91	74.5	22.2	3.3
3	$BF_3 \cdot 2H_2O$	2.50	16	67.5	53 600	95 600	1.78	75.8	20.7	3.5
4	$BF_3 \cdot 2CH_3OH$	10.0	2.5	57.2	23 500	53 950	2.30	67.8	27.7	4.5
5	$BF_3 \cdot 2CH_3OH$	5.00	2.5	80.6	68 670	157 600	2.30	69.5	26.5	4.0
6	$BF_3 \cdot 2CH_3OH$	1.25	2.5	76.6	41 000	77 900	1.90	74.8	22.5	2.7
7	$BF_3 \cdot 2CH_3COOH$	5.00	3	77.8	24 300	74 100	3.05	59.2	33.7	7.1
8	$BF_3 \cdot 2CH_3COOH$	1.25	3	76.3	61 130	275 100	4.50	62.3	32.1	5.6
9	$BF_3 \cdot 2CH_3COOH$	0.25	3	72.8	53 000	368 000	6.94	69.9	25.6	4.5

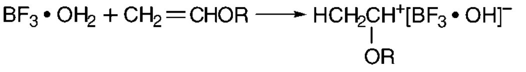
ferred to the syndiotactic propagation enthalpically, though the syndiotactic propagation is predominant entropically. In other words, the stereoregulation of tBVE polymerization with $BF_3 \cdot OEt_2$ in toluene is governed by the enthalpic factor, which is similar to the results obtained by Sumi et al.[18] for VOSi polymerization with $EtAlCl_2$ in toluene. More noteworthy fact is that the smaller value of $\Delta H_i^\ddagger - \Delta H_s^\ddagger$ for the lower concentration of $BF_3 \cdot OEt_2$ was obtained. This suggests that a new kind of propagation species generated under low $BF_3 \cdot OEt_2$ concentration has a high isospecific selectivity which leads to the most highly isotactic PVOH (PtBVE) as mentioned above.

From the kinetic study of the polymerization of alkyl vinyl ether in diethyl ether with $BF_3 \cdot OEt_2$,[19] it has been stated that the initiation of the polymerization occurs with an ion pair formed by the direct reaction between $BF_3 \cdot OEt_2$ and monomer as follows: In the polymerization system there actually exists a small amount of water; however, the exchange reaction described in eq 3 occurs and the reactions in eqs 2 and 4 seem to compete, with the initiation followed by the propagation.[7] The reaction described in eq 4 will be dominant in the polymerization reaction when the ratio of the catalyst to residual water in the reaction mixture is low. We consider that the increase in isotacticity may be caused by highly isospecific polymerization with new species generated from ligand exchange of catalyst from ether to water as shown in eq 3.



$$BF_3 \cdot OEt_2 + CH_2{=}CHOR \longrightarrow EtCH_2\underset{OR}{CH^+}[BF_3 \cdot OEt]^- \qquad (2)$$

$$BF_3 \cdot OEt_2 + H_2O \longrightarrow BF_3 \cdot OH_2 + Et_2O \qquad (3)$$



$$BF_3 \cdot OH_2 + CH_2{=}CHOR \longrightarrow HCH_2\underset{OR}{CH^+}[BF_3 \cdot OH]^- \qquad (4)$$

Effect of Water on the Polymerization. Then, we examined the polymerization in the presence of various amount of water in order to investigate the effect of water on the polymerization. The results are shown in Table 6 and Figure 5. The mm sequence fraction increased sharply only when the water/catalyst ratio was extremely reduced to as low as around 10^{-1} in the concentration range of $BF_3 \cdot OEt_2$ between 0.25 and 5.00 mol/L. However, such high water content as in run 8 in Table 6 were hardly able to promote the polymerization because water acts as a strong inhibitor or chain transfer agent. This result supports our assumption that the reaction described in eq 4 is dominant in the presence of an equimolar or greater amount of water compared to catalyst even with high catalyst concentration, which would cause a higher isospecific propagation by a new active species generated from the ligand exchange reaction according to eq 3.

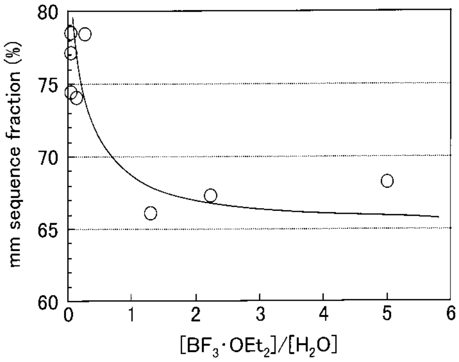


Figure 5. Effect of water on the mm sequence fraction of PVOHs derived from PtBVE prepared with $BF_3 \cdot OEt_2$ in toluene at −78 °C.

Effect of the Ligand of BF_3 Complexes on the Polymerization. As mentioned above, the mm sequence fraction increased with reducing the catalyst concentration (Figure 2), which is thought to be caused by highly isospecific polymerization with a new kind of species generated by ligand exchange from ether to water. These results suggest that the ligand of BF_3 complexes play an important role in this stereospecific polymerization. Then we studied the polymerization of tBVE with various BF_3 complexes at −78 °C in toluene. The results are shown in Table 7 and Figure 6.

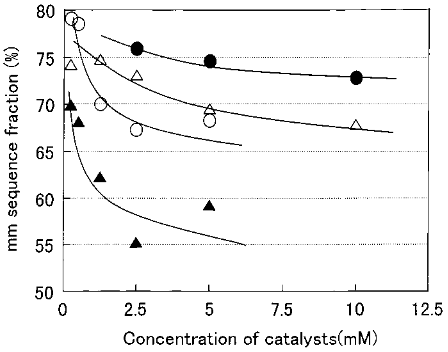
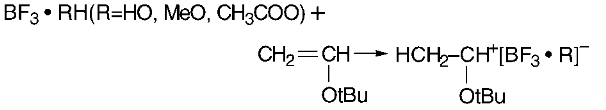


Figure 6. Effect of catalyst concentration on the mm sequence fraction of PVOHs derived from PtBVE prepared with $BF_3 \cdot OEt_2$ (○), $BF_3 \cdot 2H_2O$ (●), $BF_3 \cdot 2CH_3OH$ (△), and $BF_3 \cdot 2CH_3COOH$ (▲) in toluene at −78 °C.

In the case of $BF_3 \cdot 2H_2O$, especially at high catalyst concentrations, the polymerization system became heterogeneous by the precipitation of the resulted polymer because of the low solubility of $BF_3 \cdot 2H_2O$ in toluene, and the molecular weight of the PtBVE increased with increasing in catalyst concentration. The polymerization with $BF_3 \cdot 2CH_3OH$ proceeded homogeneously in spite of the low solubility of $BF_3 \cdot 2CH_3OH$ in toluene, and no precipitation was observed. The molecular weight of the PtBVE increased with increasing catalyst concentration, though it decreased at high concentration because a small amount of free CH_3OH seems to act as a chain transfer agent during polymerization. The polymerization with $BF_3 \cdot 2CH_3COOH$ proceeded very fast and yielded PtBVE with a relative wide distribution of molecular weight. The mm sequence fraction increased in the order $BF_3 \cdot 2CH_3COOH < BF_3 \cdot OEt_2 < BF_3 \cdot 2CH_3OH < BF_3 \cdot 2H_2O$ and increased with a reduction in the concentration for each type of catalyst.

Some models and mechanisms of isospecific propagation in homogeneous systems have been proposed for mainly vinyl ethers. Kunitake et al. proposed that important factors in controlling stereochemistry of chain growth in alkyl vinyl ether polymerization are the degree of association of growing cation and its counteranion and the physical size of the counteranion.[20,21] Steric repulsion of bulky substituents of terminal and penultimate monomer units could be minimized, and assuming a planar carbocation, a monomer attack on the same side of the counteranion (front side attack) or on the opposite side (backside attack) leads to mainly syndiotactic placement or isotactic placement, respectively. Nonpolar solvents such as toluene would be expected to favor tight association between the propagating cation and its counteranion so that they favor backside attack with formation of an isotactic configuration which minimized the steric repulsion between the bulky substituent in monomer and the growing polymer chain. Polar solvents such as CH_2Cl_2 favor inversely front side attack with formation of a syndiotactic configuration because they could stabilize separated ion pairs. These considerations suggest that the tighter association of the growing ion pair will yield the higher isotacticity at the isospecific polymerization. Kunitake et al. carried out isospecific polymerization of tBVE at −78 °C with a variety of triphenylmethyl salts as initiator, and they observed that the mm sequence fraction increased with a reduction in the counteranion size.[20] As steric hindrance between the bulky *tert*-butyl group and the counteranion may be present, the binding strength between the growing ion pair will increase with a reduction in the counteranion size, which just leads to more backside attack, that is, further isotactic-rich polymer.

The initiation reaction of cationic polymerization of vinyl ether with BF_3 complex is thought to be as follows: a direct reaction between monomer and the catalyst for $BF_3 \cdot OEt_2$ and a proton addition for BF_3 complex, whose ligand has an acidic proton, take place; the interaction between the excess ligand and growing carbenium ion can be neglected in this case because the aromatic group of toluene would interact with the chain end preferably,[15] as shown in eqs 2 (R = tBu) and 5.



$$BF_3 \cdot RH(R{=}HO, MeO, CH_3COO) + \underset{\displaystyle OtBu}{CH_2{=}CH} \longrightarrow H\underset{\displaystyle }{CH_2}{-}\underset{\displaystyle OtBu}{CH^+}[BF_3 \cdot R]^- \qquad (5)$$

The counteranions of BF_3 complexes during polymerization are thus believed to be $[BF_3 \cdot CH_3COO]^-$, $[BF_3 \cdot OEt]^-$, $[BF_3 \cdot OCH_3]^-$, and $[BF_3 \cdot OH]^-$ for $BF_3 \cdot 2CH_3COOH$, $BF_3 \cdot OEt_2$, $BF_3 \cdot 2CH_3OH$, and $BF_3 \cdot 2H_2O$, respectively. The fact that the sizes of BF_3 complexes as counteranion during polymerization shrink in the order $BF_3 \cdot 2CH_3COOH < BF_3 \cdot OEt_2 < BF_3 \cdot 2CH_3OH < BF_3 \cdot 2H_2O$ just coincides with the content of the mm sequence fraction of the resultant PtBVEs.

The mm sequence fraction increased sharply with reducing the catalyst concentration for each type of catalyst except for $BF_3 \cdot 2H_2O$ as shown in Figure 6. This is because the ligand exchange reaction from original ligand to water according to eqs 6 and 4 (R = tBu) becomes dominant with an increase in the concentration ratio of residual water, by a small amount but not zero, to the catalyst. In other words, the counteranion of the growing cation would be almost $[BF_3 \cdot OH]^-$ at low catalyst concentration irrespective of BF_3 complexes.

$$BF_3 \cdot X\ (X = MeOH, Et_2O, CH_3COOH) + H_2O \rightarrow BF_3 \cdot OH_2 + X \qquad (6)$$

Conclusion

PVOH, which has the highest isotacticity ever reported, was derived from PtBVE polymerized with $BF_3 \cdot OEt_2$ catalyst. The polymerization conditions of reduction of $BF_3 \cdot OEt_2$ concentration below 0.5×10^{-3} mol/L and an extremely low ratio of $BF_3 \cdot OEt_2$ to water of around 10^{-1} are essential factors to obtain the highly isotactic PVOH. It was suggested that a new kind of active species generated by ligand exchange reaction from ether to water could conduct more isospecific selectivity in the polymerization of tBVE.

References and Notes

(1) Fujii, K. *J. Polym. Sci., Part D* **1971**, *5*, 431.
(2) (a) Finch, C. A. *Polyvinyl Alcohol*; John Wiley & Sons: New York, 1973; Chapters 6 and 10. (b) Finch, C. A. *Polyvinyl Alcohol-Developments*; John Wiley & Sons: New York, 1992; Chapters 9 and 10.
(3) (a) Yamamoto, T.; Yoda, S.; Sangen, O.; Fukae, R.; Kamachi, M. *Polym. J. (Jpn.)* **1989**, *21*, 1053. (b) Yamamoto, T.; Yoda, S.; Sangen, O.; Fukae, R.; Kamachi, M. *Polym. J. (Jpn.)* **1990**, *22*, 636.
(4) Ofstead, R. F.; Poser, C. I. *Polym. Mater. Sci. Eng.* **1987**, *57*, 361.
(5) (a) Imai, K.; Shiomi, T.; Tezuka, Y.; Kawanishi, T.; Jin, T. *J. Polym. Sci., Part A* **1988**, *26*, 1961. (b) Imai, K.; Shiomi, T.; Tezuka, Y.; Fujioka N.; Hosokawa, T.; Ueda, N.; Fujita, K. *Kobunshi Kagaku* **1989**, *46*, 261.

(6) Murahasi, S.; Yuki, H.; Sano, T., Yonemura, U.; Tadokoro, T.; Chatani, Y. *J. Polym. Sci.* **1962**, *62*, S77.
(7) Yuki, H.; Hatada, K.; Oda, K.; Kinoshita, Murahashi, S.; Ono, K.; Ito, Y. *J. Polym. Sci. Part A-1*, **1969**, *7*, 1517.
(8) (a) Okamura, S.; Kodama, T.; Higashimura, T. *Makromol. Chem.* **1962**, *53*, 180. (b) Higashimura, T.; Suzuki, K.; Okamura, S. *Makromol. Chem.* **1965**, *86*, 259.
(9) (a) Murahashi, S.; Nozakura, S.; Sumi, M. *J. Polym. Sci. B* **1965**, *3*, 245. (b) Murahashi, S.; Nozakura, S.; Sumi, M.; Yuki, H.; Hatada, K. *J. Polym. Sci., Polym. Lett. Ed.* **1966**, *4*, 65. (c) Murahashi, S.; Nozakura, S.; Sumi, M.; Yuki, H.; Hatada, K. *Kobunshi Kagaku* **1966**, *23*, 550.
(10) Wu, T. K.; Ovenall, D. W. *Macromolecules* **1973**, *6*, 582.
(11) Ohgi, H.; Sato, T. *Macromolecules* **1993**, *26*, 559.
(12) Moritani, T.; Kuruma, I.; Shibatani, K. *Macromolecules* **1972**, *5*, 577.
(13) DeMember, J. R.; Haas, H. C.; MacDonald, R. L. *J. Polym. Sci., Polym. Lett. Ed.* **1972**, *10*, 385.
(14) Fujii, K.; Fujiwara Y.; Brownstein, S. *Prepr. 17th Polym. Symp. (Matsuyama, Jpn.)* **1968**, 1111.
(15) Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; John Wiley & Sons: New York, 1982; Chapter 4.3, p 209.
(16) Nozakura, S.; Sumi, M.; Uoi, M.; Okamoto, T.; Murahashi, S. *J. Polym. Sci.: Polym. Chem. Ed.* **1973**, *11*, 279.
(17) Fordham, J. W. L. *J. Polym. Sci.* **1959**, *39*, 321.
(18) Sumi, M.; Nozakura, S.; Murahashi, S. *Kobunshi Kagaku* **1967**, *24*, 424.
(19) Plesch, P. H. *The Chemistry of Cationic Polymerization*; Pergamon Press: New York, 1963; p 392.
(20) Kunitake, T.; Aso, C. *J. Polym. Sci., Part A*, **1970**, *8*, 665.
(21) Kunitake, T.; Takarabe, K. *Makromol Chem.* **1981**, *182*, 817.

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