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Highly isotactic poly(vinyl alcohol). III: Heterogeneous cationic polymerization of *tert*-butyl vinyl ether

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Abstract

We studied the polymerization of *tert*-butyl vinyl ether (*t*BVE) and benzyl vinyl ether with heterogeneous catalysts, that is, modified Ziegler type (Vandenberg type) catalysts and metal sulfate–sulfuric acid complexes.

Vandenberg type catalysts gave high molecular weight and *highly isotactic* poly(*t*BVE)s with relatively narrow molecular weight distribution at high temperature, and then the resultant poly(*t*BVE)s were converted into the stereoregular poly(vinyl alcohol)s (PVAs). With titanium based Vandenberg type catalyst, a relative high isotactic PVA, which has 52% triad isotacticity, was obtained from the poly(*t*BVE) polymerized at 30 °C. It was found from NMR study that the content of the triad tacticity of PVAs derived from poly(*t*BVE) catalyzed by titanium based catalysts agreed with the value calculated from the chain-end control model (Bovey's model). This fact suggests that the steric structure of the adding monomer in this system is determined by same mechanism to homogeneous BF_3 complexes catalysts system. On contrast to that, the metal sulfate–sulfuric acid complexes show significantly low activity to *t*BVE polymerization. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinyl alcohol); Isotactic; Heterogeneous cationic polymerization

1. Introduction

It is well known that vinyl ethers such as *tert*-butyl vinyl ether (*t*BVE) or benzyl vinyl ether (BzVE) has been studied as starting monomer to obtain stereoregular poly(vinyl alcohol)(PVA). Murahashi et al. [1] successfully prepared the isotactic-rich PVA by homogeneous cationic polymerization of BzVE followed by hydrolysis with hydrogen bromide (HBr). Yuki et al. [2] studied closely the relationship between the polymerization conditions of BzVE and the stereoregularity of poly(BzVE). They found that the fraction of mm sequence increased with decreasing polymerization temperature and reducing monomer concentration, and it was also influenced by polarity of the polymerization medium. On the other hand, Okamura et al. [3] reported the several works about the stereoregular polymerization of *t*BVE. They studied in detail the relationship between the polymerization conditions of *t*BVE and the stereoregularity of the obtained polymer, and isotactic-rich PVA was produced by polymerization with the homogeneous boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$) in nonpolar media under low temperature (−78 °C).

There are many reports about the stereoregular polymerization of *t*BVE or BzVE, that is, precursor of the stereoregular PVA, with homogeneous cationic catalyst, whereas heterogeneous polymerization of these vinyl ethers has not been studied well. Vandenberg reported that certain modified Ziegler type catalysts (so-called Vandenberg type catalysts) such as VCl_4–Et_3Al mixture or $TiCl_4$–Et_3Al mixture treated with $i\mathrm{Bu}_3\mathrm{Al}$–THF complex polymerize some alkyl vinyl ethers such as methyl, ethyl, *iso*butyl and *t*BVE to yield crystalline polymers [4]. It should be noteworthy that the vanadium based initiator led to highly crystalline poly(*t*BVE) at room temperature. He proposed that the stereoregular polymerization of vinyl ethers with these catalysts occurs by a cationic insertion mechanism, and the factor which controlled the steric structure of the poly(vinyl ether)s should be different from that of ordinal catalyst system such as $BF_3{\cdot}OEt_2$. However, there was no quantitative discussion about polymerization result and stereoregularity of the obtained poly(*t*BVE).

On the other hand, Higashimura et al. [5–7] and McGrath et al. found that a series of metal sulfate–sulfuric acid complexes such as $Al_2(SO_4)_3$–H_2SO_4 or $MgSO_4$–H_2SO_4

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efficiently polymerize vinyl ethers at room temperature to give crystalline isotactic polymers. They reported that the $Al_2(SO_4)_3–H_2SO_4$ catalyst yielded stereoregular poly (methyl vinyl ether) or poly(*iso*butyl vinyl ether) with higher crystallinity at room temperature than those obtained in the homogeneous polymerization with $BF_3·OEt_2$ at low temperature. Higashimura et al. [8] determined the stereoregularity of the obtained poly(methyl vinyl ether) with metal sulfate–sulfuric acid complexes by NMR spectroscopy and found that the fraction of the triad tacticity calculated from the enantiomorphic catalyst site model coincided with the experimental results. This means that only the heterogeneous catalyst, or structure of the catalyst surface, should dominate the stereoregularity of an added monomer in this catalyst and this case is entirely different from that with homogeneous BF_3 complex catalysts. However, there has been no report about the polymerization of *t*BVE or BzVE with these metal sulfate–sulfuric acid complex catalysts ever.

In the previous papers, we presented that the most highly isotactic PVA reported so far was derived from poly(*t*BVE) prepared by homogeneous cationic polymerization with $BF_3·OEt_2$ catalyst [9,10]. We also studied the polymerization of *t*BVE with various BF_3 complexes and proposed that the counter anion of the growing chain should play important roles in controlling the stereoregularity of the poly(*t*BVE) with homogeneous BF_3 complexes catalyst [10]. The heterogeneous polymerization of *t*BVE is of considerable interest for both the method to obtain the stereoregular PVAs and theoretical consideration. Then we studied the heterogeneous cationic polymerization of *t*BVE or BzVE with Vandenberg type catalysts or metal sulfate–sulfuric acid complexes. We also determined the stereoregularity of resultant PVAs derived from these poly(vinyl ether)s and discussed a mechanism for the isospecific heterogeneous polymerization on the basis of a statistical analysis of the tacticity data.

2. Experimental

2.1. Materials

Synthesis of *t*BVE monomer was carried out according to the ways described previously [10]. BzVE monomer was prepared by alkyl exchange reaction between benzyl alcohol and ethyl vinyl ether in the presence of $Hg(OAc)_2$. BzVE, *t*BVE and *iso*butyl vinyl ether (IBVE) (Tokyo Kasei Kogyo; 99%) were washed with 10% aqueous sodium hydroxide and then with water, dried overnight over potassium hydroxide (pellets), and distilled from calcium hydride before use. All solvents were purified and dehydrated carefully by the usual methods. Boron trifluoride diethyl etherate ($BF_3·OEt_2$) was purified by distillation under reduced nitrogen pressure and used as a *n*-heptane solution.

Modified Ziegler type (Vandenberg type) catalysts were prepared by the procedure described by Vandenberg [4]. The stoichiometric titanium (ST) catalyst (mole ratio of 0.34:1 $Et_3Al/TiCl_4$) was prepared under nitrogen in *n*-heptane diluent at 0.12 M concentration of $TiCl_4$ by addition of the Et_3Al. This catalyst was aged 2 h at room temperature, and then heat treated for 16 h in a 90 °C bath. This catalyst was the starting material for the pretreated stoichiometric titanium (PST) catalyst. The vanadium counterpart of ST catalyst that is the SV catalyst (0.36:1 Et_3Al/VCl_4) was prepared in the same way except of using VCl_3 as vanadium compound instead of $TiCl_4$. The PST catalyst was prepared by reacting ST catalyst with *iso*-Bu_3Al (1 M in *n*-heptane) at a mole ratio of 2:1 *iso*-Bu_3Al/Ti (0.1 M titanium concentration) for 5 min at room temperature. The pretreated stoichiometric vanadium (PSV) catalyst was prepared in a similar manner in *n*-heptane. All catalysts were handled under a moisture- and oxygen-free argon atmosphere, and dissolved in dry and distilled *n*-heptane under dry argon before use.

Metal sulfate–sulfuric acid complexes were prepared by the procedure described by Higashimura et al. [5] $Al_2(SO_4)_3·H_2SO_4$ was prepared by following method. A 12 g portion of finely powdered $Al_2(SO_4)_3–18H_2O$ and 60 ml of concentrated sulfuric acid were placed in a 100 ml flask. The mixture was stirred with a magnetic stirrer and maintained at 5 °C for 24 h and then maintained at 100 °C for 1.5 h. After cooling, it was added to 500 ml of stirred anhydrous diethyl ether. The white precipitate was filtered, washed with additional anhydrous ether and dried under vacuum. $Cr_2(SO_4)·H_2SO_4$, $MgSO_4·H_2SO_4$, $FeSO_4·H_2SO_4$ and $Fe_2(SO_4)_3·H_2SO_4$ were prepared by same method. The composition of the catalysts determined by the atomic absorption (metal composition) and ion chromatographic (SO_4^{2-}) methods corresponding to $Al_2(SO_4)_3·1.4H_2SO_4·10.4H_2O$, $MgSO_4·0.67H_2SO_4·4.0H_2O$ and $FeSO_4·0.38H_2SO_4·3.3H_2O$, respectively. All catalysts were handled under a moisture- and oxygen-free argon atmosphere, and dissolved in dry and distilled toluene under dry argon before use.

2.2. Polymerization

The polymerization of *t*BVE, BzVE or IBVE were carried out with Vandenberg type catalysts in *n*-heptane or metal sulfate–sulfuric acid complexes in toluene. An ampoule equipped with a three-way stopcock was flushed with dry nitrogen, and then the solvent and the catalyst solution were introduced with a syringe. To this catalyst solution kept at a given temperature, the monomer solution was added slowly with a syringe and the ampoule was sealed immediately. Adding a small amount of methanol that was kept 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.

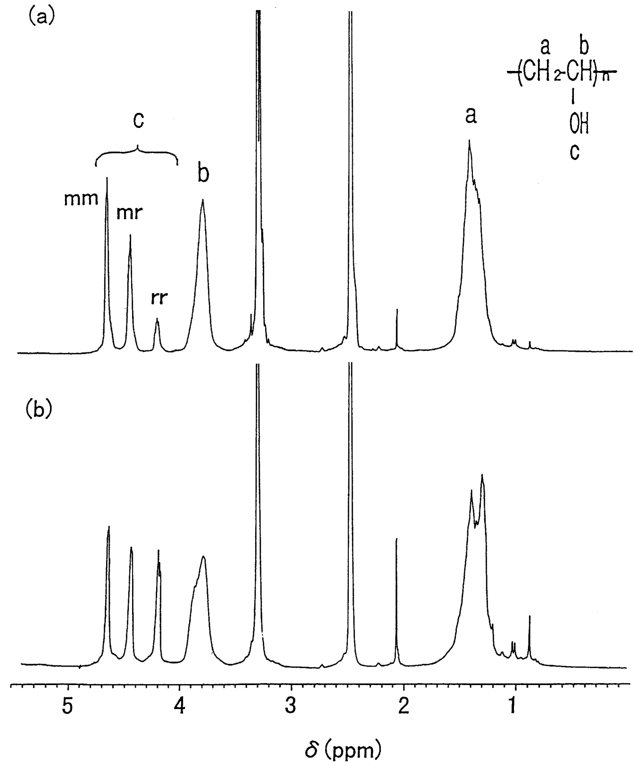

Fig. 1. ^{1}H NMR spectra of stereoregular PVAs in DMSO-d^6, at 25 °C and 270 MHz. (a) PVA obtained from the poly(*t*BVE) polymerized with PST catalyst (run 2 in Table 1); (b) PVA obtained from the poly(*t*BVE) polymerized with PSV catalyst (run 4 in Table 1). mm, mr, and rr are assigned to meso–meso, meso–racemi, and racemi–racemi sequence fraction, respectively.

2.3. Preparation of PVA from poly(tBVE)

By using HBr gases at 0 °C, poly(*t*BVE) was converted to PVA. Before dry HBr gas was passed slowly through 1–5 wt% solution of poly(*t*BVE) in 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.

2.4. Degree of polymerization measurement

The number-average molecular weight (M_n), the weight-average molecular weight (M_w) and its distribution (M_w/M_n) of polymers were measured by gel permeation chromatography (GPC) at 38 °C in THF as an eluent with Shimazu Model 802A highromatograph equipped with a differential refractometer detector. The molecular weight calibration was obtained by using 12 standard polystyrenes (Pressure Chemicals; $M_n = 580–1\ 547\ 000$; $M_w/M_n < 1.1$).

2.5. NMR measurement and tacticity determination

^{1}H NMR measurements were performed on a JEOL type GSX-270 spectrometer operating at 270.17 MHz. The spectra of PVA were measured in diethyl sulfoxide (DMSO)-d^6 at 25.0 °C. The triad tacticity of PVA can be determined by ^{1}H NMR spectrum measured in DMSO-d^6 [10,11]. Fig. 1 illustrates the ^{1}H NMR spectra of several stereoregular PVAs derived from poly(*t*BVE)s catalyzed by Vandenberg type catalysts.

3. Results and discussion

3.1. Polymerization of tBVE with Vandenberg type catalyst

In his report, Vandenberg concluded that the PSV catalyst was the Ziegler type transition metal catalyst which gave the most stereoregular polymerization [4]. So he has not studied well the polymerization of vinyl ethers with titanium based catalyst. Now, the polymerization of *t*BVE was carried out with several Vandenberg type catalysts, i.e. vanadium based catalysts and titanium based one, at 30 °C in *n*-heptane. The polymerization results are summarized in Table 1. As comparison, we also studied the polymerization of *t*BVE with $BF_3{\cdot}OEt_2$ in *n*-heptane.

The ST catalyst was a red purple dispersion and the PST

Table 1
Characterization of PVAs derived from poly(*t*BVE)s prepared with several modified Ziegler type catalysts in *n*-heptane. [*t*BVE] = 20 vol%

No.	Catalyst	[Cat.] (mM)	Temperature (°C)	Time (h)	Polymer yield (%)	Poly(*t*BVE)			PVA triad (%)		
						M_n	M_w	M_w/M_n	mm	mr	rr
1	PST	0.47	30	39	1.4	13 300	25 100	1.89	–	–	–
2	PST	1.28	30	39	25.6	12 200	23 400	1.92	52.2	38.2	9.6
3	ST	0.47	30	39	54.7	14 700	41 400	2.82	50.7	39.1	10.2
4	PSV	0.47	30	50	25.2	4000	7100	1.78	33.9	34.4	31.7
5	SV	0.47	30	50	22.6	3800	6400	1.68	35.5	32.9	31.6
6[a]	SV	0.47	30	50	32.2	8400	4800	1.75	37.0	33.0	30.0
7	VCl_3	0.47	30	50	30.0	3700	6900	1.86	32.2	36.7	31.1
8	$BF_3{\cdot}OEt_2$	0.5	0	50	0	–	–	–	–	–	–
9	$BF_3{\cdot}OEt_2$	0.5	−78	3	91.3	18 700	64 200	3.42	53.9	34.3	11.8

[a] [*t*BVE] = 50 vol%.

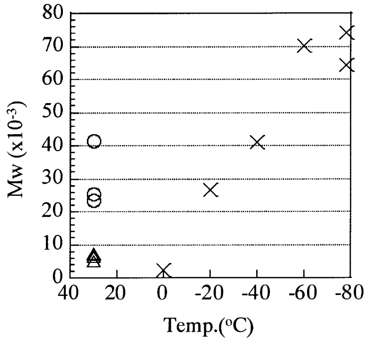

Fig. 2. Effect of polymerization temperature on the weight average of molecular weight (M_w) of poly(*t*BVE) polymerized with titanium based catalysts (circle), vanadium based catalysts (triangle) or $BF_3 \cdot OEt_2$ (cross) in *n*-heptane.

catalyst was a dark brown dispersion in *n*-heptane. The polymerization of *t*BVE with titanium based catalysts was found to be slow, and the polymer yield was in the range 30–55% polymerized for 39 h. While the rate of the homogeneous polymerization of *t*BVE with $BF_3 \cdot OEt_2$ was very fast at −78 °C, but only few amounts of the polymer was obtained at 0 °C. During the polymerization, the coloration of reaction mixture was occurred and $BF_3 \cdot OEt_2$ gave very low molecular weight poly(*t*BVE) at 0 °C and our results seem to agree with Aoshimas' founding [12]. It was very hard to recover the obtained oligomers by precipitation method because of their high solubility in methanol. Since the titanium based catalysts are insoluble in the polymerization medium, these extremely slow polymerization may be caused by some steric factor of the solid catalyst surface.

The polymerization system became heterogeneous because of low solubility of catalyst, however, the molecular weight distribution (MWD) of the polymers obtained from *t*BVE by titanium based catalysts were relatively narrow, and the GPC elution curve of polymer obtained with the titanium based catalysts showed a monomodal MWD. Higashimura et al. found a bimodal MWD of polystyrenes formed under suitable conditions, e.g. by use of acetyl perchlorate or perchloric acid in several solvents at 0 °C [13]. They studied well the nature of propagating species in cationic polymerization of styrene under various conditions and suggested that the shape of MWD were influenced by the character of the propagating species, such as the fractional contribution of the dissociated and non-dissociated propagating species to polymer formation. And all the poly(*t*BVE)s polymerized with titanium based catalysts were isolated as non-tacky, semicrystalline powdery solids. On the basis of these results, it may be suggested that the polymerization of *t*BVE proceed with a uniform active center. However, in cationic polymerization, it is known that the monomodal MWD of the polymer is not always the proof for a uniform active center because propagating species can exchange very fast each other even if more than two propagating species exist. We need further development of studies on propagating species in the polymerization of *t*BVE with titanium based catalysts to obtain more detailed information.

It is also noticeable to obtain high molecular weight polymer from *t*BVE at high temperatures. As previously reported [10], we examined the effect of temperature on the polymerization of *t*BVE with $BF_3 \cdot OEt_2$, and a marked decrease in the molecular weight of polymer was observed at higher reaction temperatures (Fig. 2). In contrast to that, especially with PST catalyst, high molecular weight of the poly(*t*BVE)s were obtained and the molecular weight of the polymer was almost constant despite the catalyst concentration. It is well known that the stability of the propagating species in cationic polymerization suppresses chain transfer, termination and other side reaction. The high molecular weight of the poly(*t*BVE) by the titanium based catalyst may be resulting from bulky and sterically hindered counter anions, which may interact with and stabilize the growing carbocation. Our results and consideration seem to be similar to the study reported by Higashimura et al. [14] for IBVE polymerization with metal sulfate–sulfuric acid complexes at room temperature.

The poly(*t*BVE)s catalyzed by the titanium based catalysts were converted into the stereoregular PVAs by hydrolysis with HBr. As shown in Fig. 1, the hydroxyl proton absorption splits three separate peaks resulting from the triad tacticity in ^{1}H NMR spectrum of the PVAs obtained from the poly(*t*BVE)s catalyzed by the titanium based catalysts. The stereoregularity of the PVAs are also summarized in Table 1. It is well known that the fraction of mm sequence of the polyvinyl ethers with BF_3 complexes increased with decreasing polymerization temperature [2,10]. However, the resultant PVAs derived from the poly(*t*BVE)s catalyzed by titanium based catalyst yielded relatively high mm sequence fraction at high temperature. The mm sequence fraction of the PVA obtained from the poly(*t*BVE) with PST catalyst is 52.2%, which is similar to that of the poly(*t*BVE) prepared with $BF_3 \cdot OEt_2$ in heptane at −78 °C. We assumed that these unusual highly stereospecific polymerization may be attributed to the isospecific species different from that of ordinary BF_3 complexes catalyst. To elucidate the reaction mechanism in more detail, the factor which controls the steric structure of an adding monomer was studied by a statistical analysis, as described later.

The vanadium based Vandenberg type catalyst did not work as well as titanium based one with *t*BVE. The polymerization of *t*BVE gave poly(*t*BVE) of lower molecular weight when catalyzed by vanadium based catalysts than when catalyzed by titanium based one.

The mm sequence fraction of the PVAs obtained from the poly(*t*BVE)s with vanadium based catalysts are 32–37%, and addition of a monomer had a little effect on the stereoregularity of the polymer (run 6 in Table 1). It is worth noting that the heterotactic PVAs were obtained from the polymerization of *t*BVE with vanadium based catalysts. These results suggest that the structure of the counter ion, which influences not only the chain transfer reaction but

Table 2
Characterization of poly(BzVE) prepared with several modified Ziegler type catalysts in *n*-heptane. [BzVE] = 20 vol%

No.	Catalyst	[Cat.] (mM)	Temperature (°C)	Time (h)	Polymer yield (%)	Poly(BzVE)			PVA triad (%)		
						M_n	M_w	M_w/M_n	mm	mr	rr
1	PST	0.47	30	39	1.7	12 800	47 000	3.67	–	–	–
2	PST	1.28	30	39	5.5	9800	31 300	3.19	–	–	–
3	ST	0.47	30	39	7.0	10 000	32 400	3.24	–	–	–
4	PSV	0.47	30	50	–	–	–	–	–	–	–
5	SV	0.47	30	50	–	–	–	–	–	–	–
6	VCl_3	0.47	30	50	–	–	–	–	–	–	–
7	$BF_3 \cdot OEt_2$	0.5	0	50	0	–	–	–	–	–	–
8	$BF_3 \cdot OEt_2$	0.5	−78	3	65.0	224 030	425 530	1.90	50.2	39.2	10.6

also the stereospecificity of the polymerization, of the system between the titanium and vanadium were different.

3.2. Polymerization of BzVE with Vandenberg type catalyst

Next, we studied the polymerization of BzVE, which is also known as starting monomer of isotactic PVA [2,15], with the titanium or the vanadium based Vandenberg type catalysts, but only few amounts of polymer were obtained (Table 2). The titanium based catalysts are slightly active in comparison with the corresponding vanadium based catalysts. Interestingly, the MWD of poly(BzVE) obtained with the titanium based catalysts was somewhat broader than that of poly(*t*BVE) with the same catalysts. This result suggests that both chain transfer reactions and different initiating and/or propagating species are present in the system. We assume the system of BzVE polymerization with the Vandenberg type catalyst is more complex than that of *t*BVE and the interaction between the benzene substituent of BzVE and the active site bound to a solid surface may influence the polymerization activity of the complete process.

We also tried to convert the poly(BzVE) which polymerized with the Vandenberg type catalysts into PVA by using several methods such as using HBr, HCl or trifluoroacetic acid. However, the obtained PVAs show gelation and brown color which may caused by small amount of the residual catalyst, and we could not estimate the accurate tacticity of the polymer.

3.3. Polymerization of tBVE with metal sulfate–sulfuric acid complexes

The polymerization of *t*BVE has been investigated in the presence of other heterogeneous catalysts based on metal sulfate–sulfuric acid derivatives. For comparison, the polymerization of IBVE has also been investigated with the same type of catalysts. As shown in Tables 3 and 4, however, all metal sulfate–sulfuric acid complexes show significantly low activity against *t*BVE polymerization compared to IBVE.

These results agree well with that reported by McGrath et al. [16]. They studied the heterogeneous cationic polymerization of several vinyl ethers and found that vinyl ethers having a linear alkyl group polymerized greatly faster than that having a branched alkyl group with the metal

Table 3
Characterization of poly(*t*BVE) prepared with several metal sulfate–sulfuric acid complexes in toluene. [*t*BVE] = 20 vol%

No.	Metal	Temperature (°C)	Time (h)	Polymer yield (%)	M_n	M_w	M_w/M_n
1	Al	0	5	0.5	15 800	32 500	2.06
2	Al	45	5	0.2	13 900	22 200	1.60
3	Al	60	5	0.1	17 400	23 200	1.33
4	Cr	0	6	0.1	34 700	81 500	2.35
5	Cr	30	5	0.3	16 800	38 700	2.30
6	Cr	60	5	0.1	18 400	25 900	1.41
7	Mg	0	6	0	–	–	–
8	Mg	30	6	0.3	870	3200	3.68
9	Mg	60	6	0.1	1700	13 000	7.65
10	Fe(II)	0	5	0	–	–	–
11	Fe(II)	30	5	0	–	–	–
12	Fe(II)	60	5	0.3	1170	2400	2.05
13	Fe(III)	−40	50	1.8	2500	9920	3.97
14	Fe(III)	−18	26	0.3	23 500	63 620	2.71
15	Fe(III)	0	5	4.7	2650	45 300	17.1
16	Fe(III)	30	5	0.3	16 420	27 570	1.68
17	Fe(III)	60	5	0.1	520	730	1.40

Table 4
Characterization of poly(IBVE) prepared with several metal sulfate–sulfuric acid complexes in toluene. [IBVE] = 20 vol%

No.	Metal	Temperature (°C)	Time (h)	Polymer yield (%)	M_n	M_w	M_w/M_n
1	Al	0	7	1.8	52 600	565 000	10.7
2	Al	45	3	48.3	71 800	828 200	11.5
3	Cr	0	7	0.2	22 200	277 000	12.5
4	Cr	60	7	20.8	466 000	1 770 000	3.80
5	Mg	0	5	11.2	17 400	109 300	6.28
6	Mg	60	5	6.2	15 200	138 000	9.08
7	Fe(II)	0	5	0.4	22 200	78 900	3.55
8	Fe(II)	60	5	6.6	690	790	1.14
9	Fe(III)	0	5	51.4	23 200	196 700	8.48
10	Fe(III)	60	5	47.5	9300	92 600	9.96

sulfate–sulfuric acid complexes, e.g. the apparent rate constant for the polymerization of *n*-butyl vinyl ether at 36 °C was about 25 times the corresponding value for IBVE. From these results, it should be indicated that the bulkiness of the substituent has greater influence on the rate of polymerization in this heterogeneous system. The bulkiness of the *t*-butyl substituent might hinder the approach to the active centers of the heterogeneous catalyst, by that significant decrease the rate of its polymerization.

3.4. Stereocontrol mechanism of tBVE polymerization with Vandenberg type catalyst

As mentioned earlier, highly isotactic PVAs were produced from poly(*t*BVE)s which polymerized with the use of the heterogeneous modified Ziegler type catalyst at high temperature. According to the NMR spectra of PVAs resulted from the poly(*t*BVE)s, these polymers contain a mm sequence fraction of more than 50%. To elucidate the reaction mechanism in more detail, the factor which controls the steric structure of an adding monomer was studied according to the same way as reported in the previous paper [8,17]. When δ_1 is defined as the persistence probability that an attacking monomer gives the same configuration (diad meso) as that of the last unit at its proceeding unit, according to Bovey and Tiers [18], the following relationships hold

$$\mathrm{mm} = \delta_1^2, \qquad \mathrm{mr} = 2\delta_1(1-\delta_1), \qquad \mathrm{rr} = (1-\delta_1)^2 \qquad (1)$$

where mm, mr and rr are a fraction of triad for isotactic, heterotactic and syndiotactic structure, respectively. On the other hand, for a system where the configuration of the monomer is determined by the catalyst, a treatment based on the enantiomorphic catalyst model was proposed by Fueno et al. [19]. In this model, each fraction of mm, mr and rr are expressed by δ_2, as shown by Eq. (2)

$$\mathrm{mm} = 1 - 3(\delta_2 - \delta_2^2), \qquad \mathrm{mr} = 2(\delta_2 - \delta_2^2), \qquad \mathrm{rr} = \delta_2 - \delta_2^2 \qquad (2)$$

where the δ_2 represents the persistence probability that a monomer adds a polymer chain end in either configuration controlled by the catalyst site.

The triad tacticity measured by NMR spectra of PVAs which obtained from the poly(*t*BVE) catalyzed by Vandenberg type catalysts is summarized in Table 1. From the observed values of the mm fraction, the value of δ_1 can be obtained by calculation from Eq. (1) and the value of δ_2 can be defined by Eq. (2). Figs. 3 and 4 show the

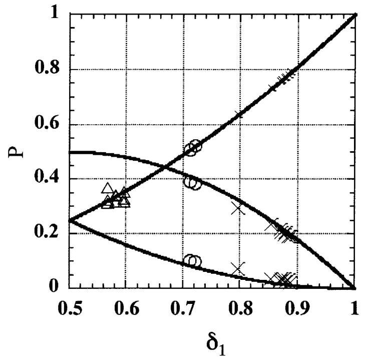

Fig. 3. Relationships between δ_1 and the probability (*P*) of the triad tacticity of PVAs obtained from the poly(*t*BVE)s catalyzed by the titanium based catalysts at 30 °C (circle), the vanadium based catalyst at 30 °C (triangle) and $BF_3 \cdot OEt_2$ at −78 °C (cross) in *n*-heptane. The curves indicate the theoretical values calculated from Bovey's model.

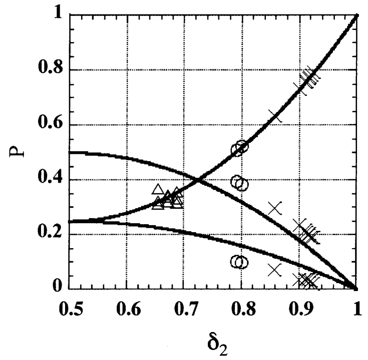

Fig. 4. Relationships between δ_2 and the probability (*P*) of the triad tacticity of PVAs obtained from the poly(*t*BVE)s catalyzed by the titanium based catalysts at 30 °C (circle), the vanadium based catalyst at 30 °C (triangle) and $BF_3 \cdot OEt_2$ at −78 °C (cross) in *n*-heptane. The curves indicate the theoretical values calculated from the enantiomorphic site model.

relationship between δ_1 or δ_2 and probability (P) of each triad tacticity of PVAs (circle for ST and PST). In Fig. 3 or 4, the P values of PVAs derived from poly(*t*BVE)s polymerized with $BF_3 \cdot OEt_2$ are also plotted against δ_1 or δ_2 for a comparison (cross). The solid lines in Figs. 3 and 4 are the theoretical values calculated from the Bovey's model (Eq. (1)) and the enantiomorphic catalyst site model (Eq. (2)), respectively. Apparently, the observed values of each fraction of the three kinds of triad (circle in Fig. 3) show significantly good agreement with the theoretical values calculated from the Bovey's model, whereas the plots of the P (circle in Fig. 4) seem inconsistent with the calculated lines from the enantiomorphic catalyst site model. This case gave good agreement with that catalyzed by homogeneous BF_3 complexes, where the growing chain end and penultimate unit control the steric structure of an approaching monomer. And this fact suggests that the steric structure of the poly(*t*BVE)s catalyzed by BF_3 homogeneous catalysts or titanium based heterogeneous catalysts was controlled by the same mechanism. These results are totally different from the results which were reported by Higashimura et al. [8]. They studied the mechanism by which the steric structure of a methyl vinyl ether monomer is controlled in the polymerization catalyzed by the sulfuric acid–aluminum sulfate complex, and found that the content of the triad tacticity of poly(methyl vinyl ether) obtained these catalysts agreed with the value calculated from the enantiomorphic catalyst site model. They confirmed that the steric structure of adding monomer in the presence of this heterogeneous catalyst is controlled only by a catalyst site. It should be reminded that different factors control the polymer configuration even in the heterogeneous polymerization if different catalyst systems are used.

In the previous papers, we presented that the most highly isotactic PVA reported so far was derived from poly(*t*BVE) prepared by cationic polymerization with $BF_3 \cdot OEt_2$ catalyst [9,10]. We also studied the polymerization of *t*BVE with various BF_3 complexes and reported that the mm sequence fraction increased in the following order: $BF_3 \cdot 2CH_3COOH < BF_3 \cdot OEt_2 < BF_3 \cdot 2MeOH < BF_3 \cdot 2H_2O$ [10]. This result suggests that the counter anion of the growing chain should play important roles in controlling the stereoregularity of the poly(*t*BVE) with homogeneous BF_3 complexes catalyst. Some models and mechanisms of isospecific propagation in homogeneous systems have been proposed for mainly vinyl ethers. Kunitake et al. [20,21] 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 counter anion, and the bulkiness of the counter anion. The 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 counter anion (front side attack) or on the opposite side (backside attack) leads to mainly syndiotactic placement or isotactic placement, respectively. Non-polar solvents such as *n*-heptane would be expected to favor tight association between the propagating cation and its counter anion so that they favor the back-side attack with a formation of 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 syndiotactic configuration because they could stabilize separated ion pairs. More recently, the stereoregulation in cationic polymerization of vinyl ethers is studied well by Sawamoto et al. [17,22,23]. It is proposed that the bulkiness and spatial shape of the counter anions are directly responsible for stereoregulation, and an effective isospecificity enhancement was demonstrated by a bulky protonic acid and/or a bulky Lewis acid from which the counter anion form. It should be noteworthy that the bulky phosphoric acid derivatives coupled with $SnCl_4$ gave highly isotactic poly(IBVE). They reported that the high isoselectivity by the phosphoric acids was probably resulting from an exchange reaction with $SnCl_4$ to generate a bulkier Lewis acid, and a bulkier counter anion can be formed during polymerization to induce isospecificity [23]. For the polymerization of *t*BVE with the titanium based catalysts, steric considerations associated with the heterogeneous nature of the catalyst play an important role in determining the mode of insertion of the monomer between the heterogeneous, and sterically hindered, counter anion and the growing polymer cation. So we concluded that the high isoselectivity by the titanium based catalyst is resulting from bulkier and sterically hindered counter anions compared to that of the polymerization with $BF_3 \cdot OEt_2$.

On the contrast, the steric configuration of PVAs obtained from the poly(*t*BVE)s with vanadium based catalysts cannot be applied to neither the Bovey's model nor the enantiomorphic catalyst site model. As shown in Fig. 3 or 4, the observed triad fraction for polymers obtained with vanadium based catalysts (triangle) do not agree with the theoretical curve calculated from these models. As an increase in the monomer concentration causes an increase of the polarity of the reaction system, the isotacticity of the polymer will be decreased. However, addition of a monomer had a little effect on the stereoregularity of the polymer (run 6 in Table 1).

This suggests that the stereochemistry of these systems follow some statistics other than chain-end control (Bovey's model) or catalyst site model. It may be difficult to elucidate the exact mechanism of the polymerization of *t*BVE with vanadium based catalysts to form isotactic polymers. It has been reported that the polymerization of *t*BVE with the PSV catalyst gave highly crystallinity polymer, but the conversion was very low [4]. Vandenberg also proposed that high molecular weight amorphous polymer obtained with the PSV catalyst may be caused by aluminum components of the system and it is difficult to avoid the contamination of the alkylaluminum component which are by-products of the PSV catalyst formation. However, all the poly(*t*BVE)s polymerized with vanadium based catalysts were isolated as non-tacky, semicrystalline powdery solids. And single symmetric GPC elution curve and relatively narrow MWD (Table 1) of poly(*t*BVE)s catalyzed by the vanadium based catalysts may suggest that polymerization of *t*BVE proceeds with a single active center, not a mixture of different polymerization species. As discussed earlier, however, the monomodal MWD of the polymer is not always the proof for a uniform active center in the cationic polymerization. We need more information about the polymerization of *t*BVE with vanadium based catalysts to elucidate the reaction mechanism in more detail.

4. Conclusions

We studied the polymerization of *t*BVE and BzVE with heterogeneous catalysts, i.e. modified Ziegler type (Vandenberg type) catalysts and metal sulfate–sulfuric acid complexes. Vandenberg type catalyst shows high activity against *t*BVE at high temperature and this result shows there is few chain transfer reaction during polymerization. The polymerization system became heterogeneous because of low solubility of catalyst, however, the MWD of the polymers obtained from *t*BVE by titanium based catalysts were relatively narrow. The mm sequence fraction of the PVA obtained from the poly(*t*BVE) with PST catalyst is 52.2%, which is similar to the poly(*t*BVE) prepared with $BF_3 \cdot OEt_2$ in heptane at −78 °C. The observed values of each fraction of the three kinds of triad show significantly good agreement with the theoretical values calculated from the Bovey's model. These suggest that the stereoregular polymerization with titanium based catalysts should occur according to chain-end control model and the high isoselectivity by the titanium based catalyst is probably due to bulkier and sterically hindered counter anions compared to that of the polymerization with $BF_3 \cdot OEt_2$.

The vanadium based Vandenberg type catalyst did not work as well as titanium based one with *t*BVE. The polymerization of *t*BVE gave poly(*t*BVE) of lower molecular weight when catalyzed by vanadium based catalysts than when catalyzed by titanium based one. The relationships between the observed triad fraction for polymers obtained with vanadium based catalysts and the theoretical curves suggested that the stereochemistry of these systems follows some statistics other than chain-end control (Bovey's model) or enantiomorphic catalyst site model.

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