Stereoregulation in Cationic Polymerization by Designed Lewis Acids. 1. Highly Isotactic Poly(isobutyl vinyl ether) with Titanium-Based Lewis Acids[1]

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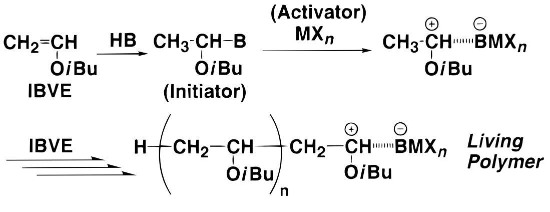
ABSTRACT: Highly isotactic-specific cationic polymerization has been achieved for isobutyl vinyl ether (IBVE) with bis[(2,6-diisopropyl)phenoxy]titanium dichloride [$TiCl_2\{OC_6H_4i\text{-}Pr_2(2,6\text{-})\}_2$ (**2**)] as a Lewis acid catalyst (activator) to be coupled with the IBVE−HCl adduct (initiator). The polymerization, homogeneous and quantitative, was carried out in *n*-hexane at −78 °C in the presence of a bulky pyridine (2,6-di-*tert*-butyl-4-methylpyridine) to give isotactic-rich polymers with a meso dyad (m) = 90−92% ($\bar{M}_n \sim 20\,000$). Under similar conditions unsubstituted counterparts ($TiCl_4$, $SnCl_4$, etc.) gave nearly atactic products ($m = 68\%$). With catalyst **2**, the isotactic content m increased at lower temperature, in less polar solvents, and with the added pyridine ($m = 64{-}92\%$). To design Lewis acids for stereoregulation, a series of titanium dichlorides [$TiCl_2(OAr)_2$] were also employed where the metal center carries two substituted phenoxy groups, and a pronounced dependence of isotacticity was observed on the bulkiness, positions, and structure of ring substituents on OAr. Overall, isopropyl groups at 2,6-positions led to the highest isotacticity, whereas bulkier or planarlike groups such as *tert*-butyl or phenyl were less effective, suggesting that not only bulkiness but also three-dimensional shapes of Lewis acids are critical in stereoregulation in cationic polymerization.

Introduction

Stereoregularity is a factor that seriously affects physical properties of polymers. Thus, stereospecific polymerizations have extensively been explored and are indeed possible for various monomers. Examples include coordination polymerization of olefins with Zieglar−Natta or metallocene catalysts[2] and anionic polymerization of methacrylates with *t*-BuMgBr and *t*-BuLi/alkylaluminum.[3] In cationic polymerization, however, stereoregularity control has been difficult, particularly in homogeneous systems although nearly complete control of molecular weight has been achieved by various living systems.[4] Effects of catalysts or counteranions, substituents of monomers, solvent polarity, and temperature on tacticity have in fact been investigated rather extensively in cationic polymerization of vinyl ethers (VE). Mechanisms have been proposed for the formation of isotactic and syndiotactic enchainments,[5,6] but very high stereospecificity is still beyond reach thus far. For example, it has been reported that BF_3OEt_2,[7] $AlEtCl_2$,[8] and $AlEt_2Cl$[8] give more or less isotactic poly(VE) in less polar solvents at low temperature, but the stereoregularity is not very high ($mm \sim 70\%$). Vinyl ethers with bulky substituents such as benzyl[9] and *tert*-butyl[10] were polymerized with BF_3OEt_2 to afford polymers of relatively high isotacticity [$mm = 86\%$ (benzyl) and 79% (*tert*-butyl)]. Allyl vinyl ether has also been polymerized by $SbCl_5$ into isotactic polymer with $m = 80\%$.[11] In addition, heterogeneous systems with aluminum sulfate and sulfuric acid give crystalline stereoregular poly(VE), where the control of stereoregularity has been made by the orientation and absorption of monomers on the surface of the catalysts.[12] However, the tacticity of the polymers was unknown because of the lack of NMR analysis at that time.

More recently, we have developed a series of living cationic polymerizations of vinyl ethers, styrene derivatives, and related monomers (eq 1), which are almost invariably initiated by binary systems consisting of a protonic acid (HB; initiator) and a Lewis acid (MX_n). A Lewis acid acts as a catalyst/activator that interacts with the terminal covalent bonds (∼∼C−B) derived from initiator HB and thereby induces its reversible dissociation into a growing carbocation. Via this dissociation, in turn, the Lewis acid combines with the anionic part (B) of the terminal to form the counteranion $B{-}MX_n^-$, which associates with the growing carbocation, by one way or another, and thus affects the nature of the active species. In the course of these studies, we have in fact noted that the judicious choice of the Lewis acids is crucial in achieving living cationic polymerization or precise control of the propagation process. In particular, a series of titanium chlorides and alkoxides, $Ti(OR)_nCl_{4-n}$ (R = alkyl or aryl), are quite useful in that, by changing the number (n) and the structure of the alkoxyl or aryloxyl substituents (OR), one can systematically control (and thus design) their Lewis acidity and in turn the nucleophilicity of the counteranions.[13] For vinyl ethers, the dichlorides such as $TiCl_2(Oi\text{-}Pr)_2$ and $TiCl_2(OPh)_2$ proved most efficient and of suitable Lewis acidity to effect living cationic polymerization.



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B: I, Br, Cl, $OCOCF_3$, etc.
MX_n: $ZnCl_2$, $SnBr_4$, $TiCl_2(OiPr)_2$, etc.

From these findings we then note, relative to the stereoregulation of cationic polymerization, that such features of the HB/MX_n binary initiating systems would be advantageous, because one could control the stere-

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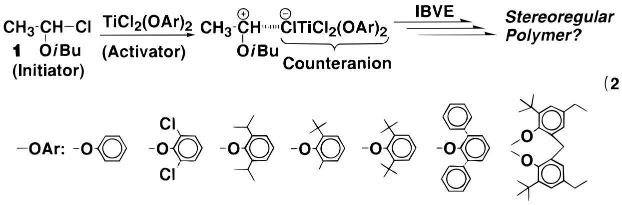
ochemical environment of the growing carbocation through designing the Lewis acid components that determine the bulkiness, topology, and electronic nature of the associating counteranion. To our knowledge, such a Lewis acid-based approach to the counteranion design is unprecedented, neither in efforts for stereoregulation of cationic polymerization nor in fundamental studies of its stereochemistry. For example, in their now classical work, Higashimura[5] and Kunitake[6] were indeed aware of the importance of counteranions in determining, at least in part, the steric course of vinyl ether polymerizations, but their primary attention was apparently directed to the ionic radii and average charge density of counteranions. Therefore, they mostly employed simple spherical counteranions derived from a series of metal halides where the central metals alone were systematically varied. However, these studies led to important knowledge that isotactic propagation is preferred in ion-pair growing ends, i.e., in nonpolar solvent and with suitably bulky counteranions.

In this work, the first of our series, we therefore examined the possible stereoregulation of cationic polymerization by employing a series of titanium dichlorides [TiCl$_2$(OAr)$_2$] for which the bulkiness, topology (spatial shape), and electronic nature of counteranions can be manipulated by designing the structure of the aromatic substituents OAr (eq 2). Herein we employed a series of bulky titanium compounds, 2,6-disubstituted TiCl$_2$(OAr)$_2$, for the cationic polymerization of isobutyl VE (IBVE) in conjunction with adduct **1** (eq 2). Our preliminary results show that the tacticity of poly(IBVE) depends on the substituents of the titanium compounds.[14] In this paper, we report that bis(2,6-diisopropylphenoxy)titanium dichloride gives highly isotactic poly(IBVE) (m = 90−92%, mm = 83%) in *n*-hexane at −78 °C in the presence of a bulky pyridine additive (2,6-di-*tert*-butyl-4-methylpyridine, DTBMP).



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Results and Discussion

Cationic Polymerization of IBVE with Substituted TiCl$_2$(OAr)$_2$. IBVE was polymerized with various 2,6-disubstituted phenoxytitanium(IV) dichlorides [TiCl$_2$(OAr)$_2$] in conjunction with the HCl adduct of IBVE (**1**) in toluene at −78 °C. The ring substituents have been selected in terms of their bulkiness and shape, along with their electronic nature. Figure 1 shows conversion−time curves of the polymerizations and size-exclusion chromatograms (SEC) of the polymers obtained with various titanium compounds. The polymerization rate depends on the substituents; with the 2,6-dichlorophenoxy titanium compound, which has electron-withdrawing chloro atoms on the phenoxy group, the polymerization occurred very fast and was completed in 1 min. On the other hand, the polymerization was very slow with the corresponding 2,6-diphenylphenoxide, which has two bulky substituents on the phenoxy group. These results show that the nature of 2,6-substituents on the phenoxy groups of the titanium compounds has great effects upon the polymerizations.

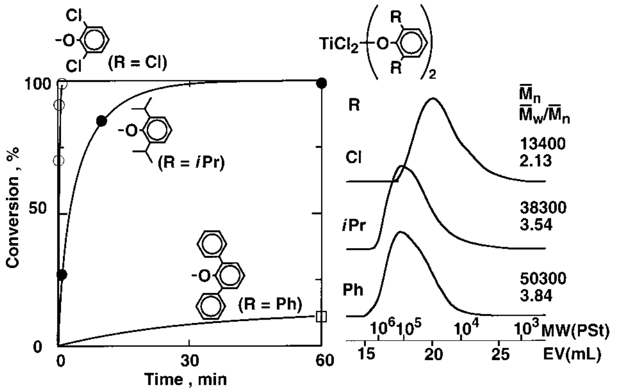

Figure 1. Polymerization of IBVE with **1**/TiCl$_2$(OAr)$_2$ in toluene at −78 °C: $[M]_0$ = 0.38 M; $[\mathbf{1}]_0$ = 5.0 mM; $[TiCl_2(OAr)_2]_0$ = 10 mM. 2,6-Substituent (R) on OAr: R = Cl (○); *i*Pr (●); Ph (□).

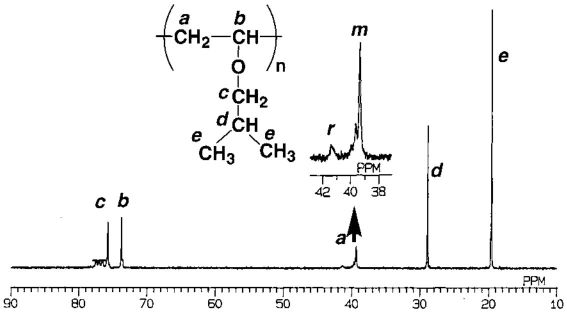

Figure 2. ^{13}C NMR spectrum (67.9 MHz) of poly(IBVE) in CDCl$_3$ at 55 °C. Polymerization conditions: $[M]_0$ = 0.38 M; $[\mathbf{1}]_0$ = 5.0 mM; $[TiCl_2\{OC_6H_3i\text{-}Pr_2(2,6\text{-})\}_2]_0$ = 10 mM, in toluene at −78 °C.

The number-average molecular weights ($\bar{M}_n$) were larger than the calculated values, and the molecular weight distributions (MWDs) were broad. These titanium compounds with substituted phenoxide groups were not effective in living polymerization. Such substituents on the phenoxy group near the titanium center may prevent effective interaction between the terminal chloride and the metal due to the steric hindrance, which results in slow interconversion between the dormant and the active species and broad MWDs.

Steric Structure of Poly(IBVE) with TiCl$_2$(OAr)$_2$. As shown in the representative ^{13}C NMR spectrum of a sample obtained with TiCl$_2${OC$_6$H$_3$*i*-Pr$_2$(2,6-)}$_2$ (**2**), the dyad distributions of poly(IBVE) can be determined from the peak intensity ratios of the main chain methylene carbons [−*C*H$_2$−CH(O*i*Bu)−] around 39−42 ppm where the meso (m) and racemo (r) dyads are well-resolved (Figure 2).[14] The absorptions of the methylene carbons [−O*C*H$_2$−CH(CH$_3$)$_2$] around 76−77 ppm can be used for the determination of triad distributions, but the signals of CDCl$_3$ at 77 ppm prevent the precise integrations of these peaks. Spectra of some samples were thus recorded in C$_6$D$_6$ especially for the determination of triad distributions (see below).

Figure 3 compares the partial ^{13}C NMR spectra for the main chain methylene signals for a series of poly(IBVE) samples obtained in toluene with titanium tetrachloride and four TiCl$_2$(OAr)$_2$ derivatives with 2,6-disubstituted phenoxy groups [OAr = O−C$_6$H$_3$Y$_2$(2,6-); Y = C$_6$H$_5$, *tert*-Bu, Cl, *i*-Pr]. Except for the difference in Lewis acids, all of the samples were prepared under the same conditions (see Figure 1, caption). The dyad meso/racemo (m/r) peak ratios and the peak width clearly

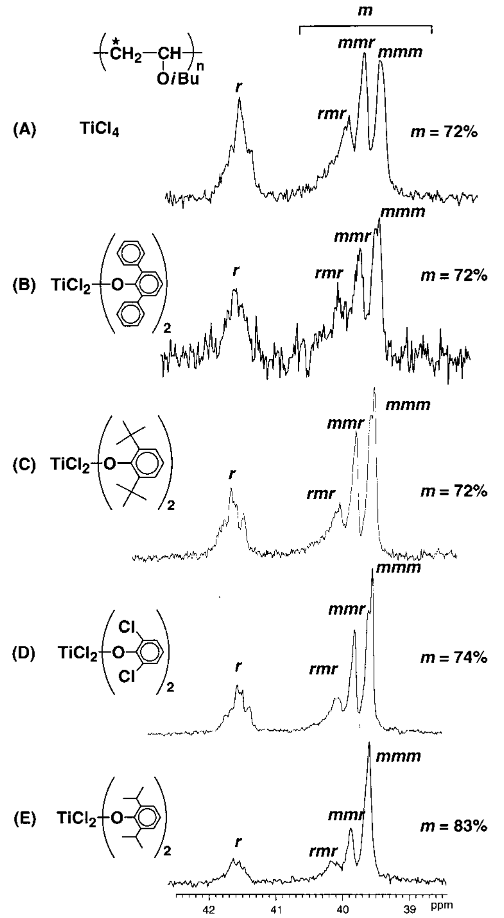

Figure 3. ^{13}C NMR spectra (67.9 or 125.8 MHz, $CDCl_3$, 55 °C) around 39−42 ppm of poly(IBVE) obtained with **1**/MX_n at −78 °C: (A) $[M]_0 = 0.38$ M, $[\mathbf{1}]_0 = 5.0$ mM, $[TiCl_4]_0 = 2.0$ mM, in toluene; (B)−(E) $[M]_0 = 0.38$ M, $[\mathbf{1}]_0 = 5.0$ mM, $[MX_n]_0 = 10$ mM, in toluene.

changed with the Lewis acids. Namely, in all cases the meso signal is predominant over the racemo counterpart, but the meso dyad was rather low (72%) of the unsubstituted form ($TiCl_4$) and even for the derivatives with very bulky ring substituents ($Y = C_6H_5$, *tert*-Bu) (Figure 3A−C). Thus, the introduction of bulky groups on the 2,6-positions of the OAr seems not generally effective, relative to $TiCl_4$, in controlling stereochemistry of the vinyl ether propagation.

In contrast, the isopropyl form (Y = *i*-Pr; Figure 3E), whose 2,6-substituents are less bulkier than phenyl or *tert*-butyl, gave clearly larger and sharper meso signals to give $m = 83\%$, the highest among the seven $TiCl_2(OAr)_2$-type Lewis acids employed herein under these conditions (see also below). When compared with those for $TiCl_4$ and the phenyl or *tert*-butyl counterparts, the spectral changes are much clearer than that in the rather insensitive numerical meso values: the three meso signals for the isopropyl form are sharper, the *mmm* peak is particularly predominant, and the racemo peak is very small.

These trends demonstrate that the 2,6-disubstituted phenoxy rings are effective in facilitating the meso propagation but that the bulkiness of the substituent Y [in $-OC_6H_3Y_2(2,6\text{-})$], or the OAr groups in general, is not a primary factor. This point can be better illustrated in Figure 4, which shows the computer-generated space-filling molecular models of the seven $TiCl_2(OAr)_2$ derivatives and their parent form $TiCl_4$, along with the meso contents of the polymer samples obtained from them (under the same conditions as for those in Figure 3). The models are generated by a molecular mechanics program (MM2) where the conformation is optimized in bond length and bond angle so as to minimize strain energy. In the figure they are shown edge-on in terms of the dihedral plane for the Cl−Ti−Cl bonds; the Ti center is seen behind the two chlorines. In all cases the $TiCl_2$ part is fairly well exposed for the interaction with the terminal chlorine in generating the carbocationic growing species.

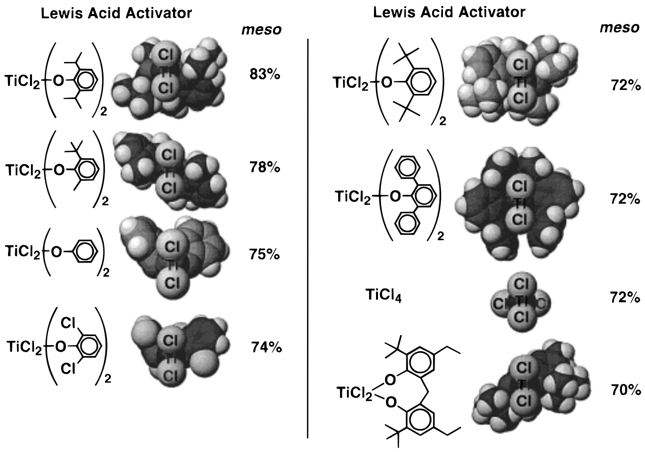

Figure 4. Meso dyad contents of poly(IBVE) obtained with **1**/MX_n in toluene at −78 °C and computer-generated molecular models of titanium compounds. Polymerization conditions: $[M]_0 = 0.38$ M; $[\mathbf{1}]_0 = 5.0$ mM; $[TiCl_2(OAr)_2]_0 = 10$ mM (2.0 mM only for $TiCl_4$).

Obviously, the titanium center becomes more sterically hindered when bulkier 2,6-substituents (Y) are attached on the phenoxy groups. Rather unexpectedly, however, the highly bulky forms with Y = phenyl or *tert*-butyl resulted in rather low meso contents ($m = 72\%$) without appreciable changes from the results for the least bulky parent $TiCl_4$. Along with another bulky derivative with a bridged bisphenoxy group ($m = 70\%$), these crowded Lewis acids appear to form counteranions too bulky for effective stereoregulation. Note that they in fact induced very slow polymerizations only (cf. Scheme 1), probably too bulky to effectively interact with the terminal chlorine, either.

The diisopropyl form (**2**), which gave the highest meso content among the seven acids, appears less bulky (Figure 4, top left). However, inspection of its molecular model indicates that the isopropyl groups are twisted relative to the aromatic ring, and because of this the space around the titanium center is even more sterically hindered than in the *tert*-butyl or phenyl derivatives. Apparently, a similar steric environment can be seen for the 2-*tert*-butyl-6-methyl form, which also gave a relatively high meso value (78%).

These results suggest that stereoregulation is affected by not only the overall bulkiness of the Lewis acid or its substituents but also other factors, such as the spatial shape and symmetry around the Lewis acid's metal center from which the counteranion is formed by attaching a chlorine of the dormant terminal. The latter spatial factor is therefore expected to affect the bulkiness and spatial shape of the resulting counteranions, which interact with the cationic growing site and is directly responsible for stereoregulation. Further studies are needed along this line.

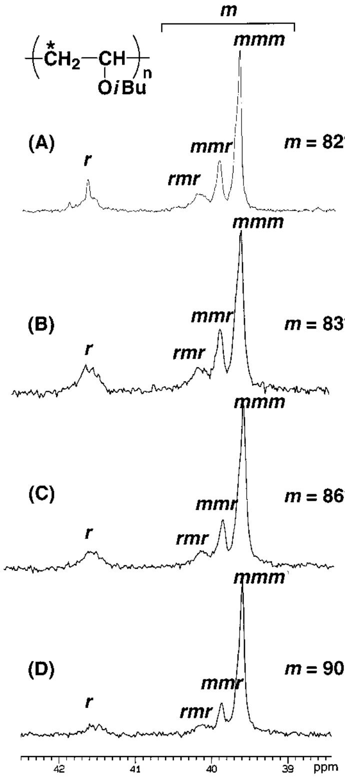

Figure 5. ^{13}C NMR spectra (67.9 or 125.8 MHz, $CDCl_3$, 55 °C) around 39−42 ppm of poly(IBVE) obtained with **1**/**2** at −78 °C: (A) $[M]_0 = 0.38$ M, $[\mathbf{1}]_0 = 5.0$ mM, $[\mathbf{2}]_0 = 10$ mM, in CH_2Cl_2; (B) $[M]_0 = 0.38$ M, $[\mathbf{1}]_0 = 5.0$ mM, $[\mathbf{2}]_0 = 10$ mM, in toluene; (C) $[M]_0 = 0.38$ M, $[\mathbf{1}]_0 = 5.0$ mM, $[\mathbf{2}]_0 = 10$ mM, in *n*-hexane; (D) $[M]_0 = 0.38$ M, $[\mathbf{1}]_0 = 5.0$ mM, $[\mathbf{2}]_0 = 10$ mM, $[DTBMP]_0 = 2.0$ mM, in *n*-hexane.

Highly Isotactic Poly(IBVE): Effects of Reaction Conditions. The steric course of propagation will be affected by interaction of the counteranion with the growing carbocation, and the interaction, in turn, will be a function of not only the counteranion structure but also reaction conditions such as solvent polarity and temperature. We thus examined the effects of these conditions on the IBVE polymerization with the Lewis acid **2** $[TiCl_2\{OC_6H_3i\text{-}Pr_2(2,6\text{-})\}_2]$, which proved most isotactic-selective among the seven Lewis acids so far discussed. The results are summarized in Figure 5 (^{13}C NMR; the main-chain methylene region) and Table 1 (meso dyad data).

As in the usual cationic polymerization, the meso contents increased with decreasing solvent polarity (CH_2Cl_2 < toluene < *n*-hexane; Figure 5A−C; Table 1, entries 1−3), and the value for hexane exceeded that for toluene (86% vs 83%). This is due to the suppression of ionic dissociation of the growing carbocation.

Addition of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP), known as a hindered base or as a proton trap, increased the meso dyad value, especially 90% in *n*-hexane (Table 1, entry 5, and Figure 5D). The effects of DTBMP are probably ascribed to the suppression of the initiation from the adventitious water that would generate hydroxide-based less nucleophilic counteranions or to possible interaction between DTBMP and the growing species.

All the polymerizations thus far investigated were initiated by the addition of **2** into the solution of monomer and **1** in *n*-hexane at −78 °C. To diminish the polar effects of the vinyl ether monomer, we also examined the polymerization initiated by slow addition of IBVE into the solution of **1** and **2** in *n*-hexane at −78 °C (Table 1, entry 6). This procedure gave higher meso content (92%). The triad distribution (*mm*) was 83%, the highest value for poly(IBVE) to our knowledge.

Effects of temperature were investigated where the polymerizations were carried out at −15 °C in the presence of DTBMP (Table 1, entries 7 and 8). The stereoregularity is decreased by increasing the temperature as in usual ionic polymerizations. However, the molecular weight distributions were narrower, and the molecular weight increased with conversion, which suggests the occurrence of living polymerization.

DSC Analysis of the Isotact-Rich Poly(IBVE). The formation of isotact-rich poly(IBVE) with $m \geq 90\%$ promoted us to investigate the thermal property of the polymer by differential scanning calorimetry (DSC). We thus used the isotact-rich polymer (Table 1, entry 6: $m = 90\%$, $\bar{M}_n = 32\,100$, $\bar{M}_w/\bar{M}_n = 2.12$) and the atactic polymer ($m = 68\%$, $\bar{M}_n = 33\,200$, $\bar{M}_w/\bar{M}_n = 1.16$) obtained by the living cationic polymerization **1**/$SnCl_4$/*n*-Bu_4NCl systems at −15 °C in CH_2Cl_2,[16] where both the $\bar{M}_n$ were about 3×10^4. Both samples showed an endothermic bias at −14 °C due to glass transition, whereas another endothermic peak, probably arising from melting, was different in the two; the isotact-rich poly(IBVE) showed this peak at 131 °C whereas the atactic poly(IBVE) at 47 °C. There is also difference in appearance, where the former was a stiff film and the latter was a soft semisolid. These results show that soft and adhesive character of poly(VE) can be changed by tacticity of polymers, which may lead to new character of poly(VE) as materials.

In conclusion, control of stereoregularity in cationic polymerization can be achieved by the Lewis acid-type activators based on their substituents. Especially, bis(2,6-diisopropylphenoxy)titanium dichloride (**2**) gave isotact-rich ($m \geq 90\%$) poly(IBVE) in *n*-hexane at −78 °C in the presence of DTBMP in conjunction with **1**.

Experimental Section

Materials. IBVE (Tokyo Kasei; purity >99%) was washed with 10% aqueous sodium hydroxide and then with water, dried overnight over potassium hydroxide (pellets), and distilled twice over calcium hydride before use. Toluene, *n*-hexane, and CH_2Cl_2 (solvents) and carbon tetrachloride (an internal standard for gas chromatography) were purified by the usual methods and distilled twice over calcium hydride before use. $TiCl_4$ (Aldrich, >99%) was used as received. 2,6-Diisopropylphenol (Tokyo Kasei, >98%), 2,6-di-*tert*-butylphenol (Wako, >98%), 2,6-dichlorophenol (Aldrich, >99%), 2,6-diphenylphenol (Aldrich, >98%), 2-*tert*-butyl-6-methylphenol (Tokyo Kasei, >95%), and 2,2′-methylenebis(6-*tert*-butyl-4-ethylphenol) (Aldrich, >90%) were used as received for the preparation of $TiCl_2(OAr)_2$ as below. All the 2,6-disubstituted phenoxytitanium(IV) dichlorides $[TiCl_2(OAr)_2]$ except $TiCl_2(OPh)_2$ were prepared as below. $TiCl_2(OPh)_2$ was prepared and purified as already reported.[12]

Preparation of $TiCl_2(OAr)_2$. All the procedures were carried out under dry argon in baked glassware equipped with three-way stopcocks. All the solvents were used after purification and distillation. All the 2,6-disubstituted phenoxytitanium(IV) dichlorides $[TiCl_2(OAr)_2]$ were prepared by stirring titanium(IV) chloride and corresponding 2 equiv of 2,6-disubstituted phenol under argon flow to remove the produced HCl gas. For example, **2** was prepared as below. Titanium(IV) chloride (2.6 mL, 23.7 mmol) was added dropwise to a solution of 2,6-diisopropylphenol (8.8 mL, 47.2 mmol) via a dry syringe in CH_2Cl_2 (30 mL) at −30 °C. On addition of $TiCl_4$, HCl gas was generated, which was trapped by bubbling into

Table 1. Effects of Solvent Polarity, Additive, and Temperature on Cationic Polymerization of IBVE with 2[a]

entry	temp, °C	solvent	additive	conv, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	meso, %
1	−78	CH_2Cl_2	none	98	10 100	2.56	82
2	−78	toluene	none	99	38 300	3.54	83
3	−78	*n*-hexane	none	93	23 800	3.43	86
4	−78	toluene	DTBMP	95	36 400	2.32	89
5	−78	*n*-hexane	DTBMP	95	47 400	1.93	90
6	−78	*n*-hexane	DTBMP	97	32 100	2.12	90
7[b]	−78	*n*-hexane	DTBMP	80	19 400	2.56	92
8	−15	CH_2Cl_2	DTBMP	98	5 800	1.28	64
9	−15	toluene	DTBMP	98	12 100	1.12	71

[a] $[M]_0 = 0.38$ M; $[\mathbf{1}]_0 = 5.0$ mM; $[\mathbf{2}]_0 = 10$ mM; $[DTBMP]_0 = 0$ or 2.0 mM. [b] The polymerization was carried out via addition of IBVE into the mixture of **1**, **2**, and DTBMP in *n*-hexane at −78 °C.

a 10% NaOH solution. After stirring at −30 °C for 10 min, the mixture was stirred at room temperature for 1 h. After the solution was evacuated by vacuum pump, the reddish-brown liquid remained and then dissolved in toluene. The solution was sealed in brown ampules and stored in the dark in a freezer. **2** was also prepared by another method where equimolar $TiCl_4$ and $Ti(OAr)_4$ were mixed together.

Synthesis of HCl−IBVE Adduct (1). The HCl−IBVE adduct **1** was synthesized by bubbling dry HCl gas through a solution of IBVE (9.0 mL of IBVE in 60 mL of *n*-hexane; 1.0 M) at −78 °C. The gas was generated by dropping concentrated sulfuric acid into powdery sodium chloride and dried by passing it through a column packed with calcium chloride. After 30 min, the excess HCl in the reaction mixture was removed by bubbling dry nitrogen gas at 0 °C for 30 min, and the clean and quantitative formation of adduct **1** was confirmed by ^{1}H NMR spectroscopy. The concentration of **1** was determined by titrating the chloride by the Volhard method; the observed value (~1 M) further confirmed the quantitative formation of **1** from IBVE.

Polymerization Procedures. Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure in toluene is given below: The reaction was initiated by sequential addition of prechilled solutions of **1** (in *n*-hexane, 0.30 mL) and titanium complex (in toluene, 0.30 mL) via dry syringes into a monomer solution (in toluene, 2.4 mL) containing IBVE (0.15 mL) and CCl_4 (0.15 mL). After predetermined intervals, the polymerization was terminated with prechilled methanol (2.0 mL) containing a small amount of ammonia. Monomer conversion was determined from its residual concentration measured by gas chromatography with CCl_4 as an internal standard. The polymer yield by gravimetry was in good agreement with the gas-chromatographic conversion of the monomer.

The quenched reaction mixture was washed with dilute hydrochloric acid, aqueous sodium hydroxide solution, and then with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymers.

Measurements. The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ ratios of the polymers were measured by size-exclusion chromatography (SEC) in chloroform on three polystyrene gel columns (Shodex K-805L × 3) that were connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index detector. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemicals; $\bar{M}_n = 580{-}1\,547\,000$; $\bar{M}_w/\bar{M}_n \leq 1.1$) as well as the monomer. ^{1}H and ^{13}C NMR spectra of the produced polymers were recorded in $CDCl_3$ or CCl_4/C_6D_6 (9/1 v/v) at 55 °C on a JEOL LNM-LA500 or a JEOL JNM-GSX270 spectrometer, operating at 500.2 or 270.2 MHz (^{1}H) and 125.8 or 67.9 MHz (^{13}C), respectively. The DSC measurements were performed on a Thermal analyzer system WS002 (MAC Science, Tokyo) equipped with a TAPS1000S control unit and a DSC3100S module. Polymer solid samples (ca. 8 mg) were measured in an aluminum container under a dry nitrogen flow at a heating or cooling rate of 10 °C/min. α-Alumina was used as a standard.

The Computer-Generated Molecular Models of the Titanium Compounds. Molecular mechanics were carried out using the CAChe system (CAChe Scientific) to optimize the titanium compounds. MM2 parameters were used as force field parameters, and optimization was done by conjugate gradient method until the convergence energy became less than 0.001 kcal/mol. The molecular model with the lowest energy was determined by generating an exhaustive potential energy map computed from dihedral search labels for all the single bonds searching between −180° and 120° in five steps and all the double bonds searching between −180° and 90° in three steps, followed by picking up 10 conformers from the one with the lowest energy and further optimization of them.

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References and Notes

(1) This work was presented in part at the 46th Annual Meeting of the Society of Polymer Science, Tokyo, Japan, May 1997; Paper IPe025. Ouchi, M.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1997**, *46* (1), 167.
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