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Aromatic Acetals as New Initiators for Cationic Polymerization of Isobutyl Vinyl Ether[1]

Kotaro Satoh, Masami Kamigaito, and Mitsuo Sawamoto*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

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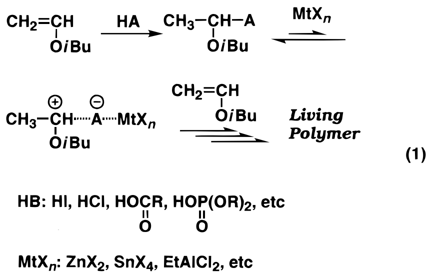
ABSTRACT: A series of aromatic acetals (**1**) from substituted phenols [$CH_3CH(O\textit{i}Bu)OAr$; Ar = C_6H_5, *p*-$CH_3OC(O)C_6H_4$, *p*-$CH_3C(O)C_6H_4$, *p*-$NO_2C_6H_4$, 4-NO_2-2,6-di-C_6H_5−C_6H_2, *o*-$CH_3C(O)C_6H_4$] were employed as new initiators in conjunction with Lewis acids (MtX_n) for the living cationic polymerization of isobutyl vinyl ether (IBVE). Most of them were quantitatively synthesized by the addition of the corresponding phenols to IBVE. When coupled with aluminum chloride ($AlCl_3$), **1** gave polymers with broad molecular weight distributions (MWDs), whereas the addition of ethyl acetate (10 vol %) to these systems led to the formation of controlled polymers whose number-average molecular weights ($\bar{M}_n$) were directly proportional to monomer conversion, with relatively narrow distributions ($\bar{M}_w/\bar{M}_n \sim 1.2$). The aromatic acetals in conjunction with tin halides (SnX_4; X = Cl, Br) gave relatively high meso contents (81%) in toluene at −78 °C.

Introduction

Living cationic polymerization[2] of vinyl monomers has permitted precise control of the number-average molecular weight ($\bar{M}_n$), molecular weight distribution (MWD), and other structural factors of polymers formed by cationic polymerizations. Along with this development, a wide variety of initiating systems have been developed, most of which are combinations of a protonic acid (HA) and a Lewis acid (MtX_n) (eq 1).[3−6] The former (or its adduct with a vinyl monomer) serves as an initiator to form a dormant carbon−halogen or related covalent linkage (∼∼C−A) and the latter as a catalyst or an activator to generate a carbocationic growing species therefrom and thus to trigger controlled propagation. Despite the generality of this approach and the fairly wide range of protonic acids that are available for achieving living cationic polymerization, the scope of the anionic part A has been confined to be primarily to halogens, carboxylates, and phosphates, rendering fine regulation of the chemical and steric nature rather difficult.[5] This is a reason in part why we have made some efforts to design the Lewis acids, rather than protonic acids, for living cationic polymerization adaptable to various monomers[3] and for possible stereoregular polymerization.[7]



(1)

We have recently focused our attention on the reaction that a series of substituted phenols undergo electrophilic addition onto alkyl vinyl ethers (VEs) to give the corresponding aromatic acetals (**1**) (Scheme 1).[1] While mechanistically very similar to those of hydrogen halides[8] and carboxylates,[4,5] the addition reactions have turned out to be surprisingly facile and selective, just proceeding quantitatively upon heating a mixture of the two reactants, despite the fact that phenols are much weaker protonic acids than hydrogen halides (Chart 1).[9]

Scheme 1

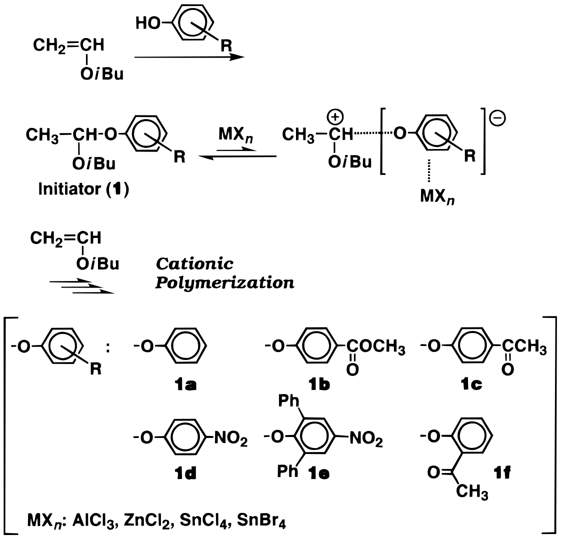
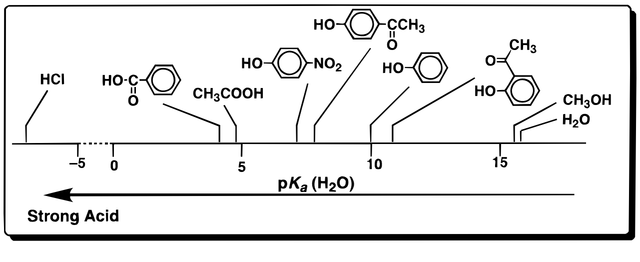


Chart 1. pK_a Values (25 °C, in H_2O) of Phenol Derivatives and Some Protonic Compounds



Aliphatic acetals [$CH_3CH(OR^1)(OR^2)$; R^1, R^2 = alkyl] are well-known as precursors of carbocations under acidic conditions. However, they have rarely been

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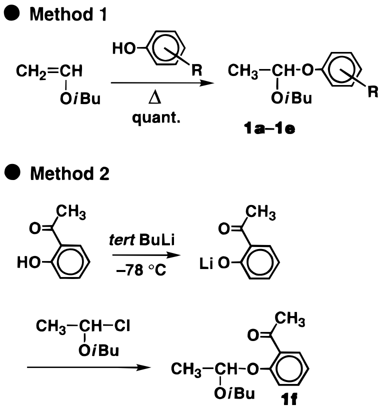
employed as initiators for cationic polymerization, where the cation formation apparently involves a series of side reactions such as dealcoholation. To avoid these, the moderation of the growing species by an electrophile was required.[10] Much less attention has been paid to aromatic acetals such as **1**, probably because of the strong C−OAr bond that is difficult to generate cationic species under usual cationic polymerization conditions. On the other hand, relative to the aliphatic counterparts, these aromatic acetals seem to permit fine structural tuning and manipulation of their aryloxide counteranions, particularly in terms of electronic nature (nucleophilicity) and steric environment, by simply introducing a variety of substituents into the aromatic rings.[11]

In this work we synthesized the new aromatic acetals (**1a**−**1f**) (Scheme 2) and employed them as new initiators for living cationic polymerization of isobutyl vinyl ether (IBVE) (Scheme 1). In the presence of a Lewis acid, the carbon−aryloxide linkage will be dissociated to give the vinyl ether carbocation and the aryloxide anion, the nucleophilicity and steric bulkiness of which will be modulated by the ring substituent(s). We report here that the initiators **1**, coupled with AlCl$_3$ as a Lewis acid, induce the controlled cationic polymerization of IBVE.

Scheme 2



Results and Discussion

1. Synthesis of Aromatic Acetals. Prior to polymerizations, we examined the synthesis of the aromatic acetals (**1a**−**1f**), which would be initiators as well as model compounds for the dormant polymer terminals with carbon−aryloxide (C−OAr) groups (Scheme 2). As reported in previous papers,[5] the adducts of a vinyl ether and a protonic acid have been synthesized by simple addition reactions. Similarly, upon heating, most of the phenol derivatives reacted quantitatively with IBVE to form the related aromatic acetals (**1a**−**1e**) (method 1 in Scheme 2). However, *o*-acetylphenol did not react directly, because of its low acidity caused by the intramolecular hydrogen bonding of the acidic proton. The adduct (**1f**) was then prepared by the substitution reaction of the IBVE−HCl adduct with the lithium salt of the phenol (method 2).

Figure 1 shows the representative ^{1}H NMR spectra of the aromatic acetals thus prepared (**1a**, **1d**, and **1e**). Every spectrum showed a quartet at 4.5−5.5 ppm (b), assigned to the methine proton of the adduct, and these spectra confirm the quantitative and selective formation of the aromatic acetals. For a series of para-substituted phenols (**1a**−**1d**), the methine peak shifted to upfield regions as the pK_a values of the starting phenols decreased (Table 1). This suggests that the methine group of the IBVE unit (i.e., the potential carbocationic site) becomes more electron deficient with an increase in the acidity of the phenols. On the other hand, the methine signal of *o*-acetylphenol adduct (**1f**) appeared at 5.54 ppm, almost at the same downfield position as for the *p*-acetylphenol adduct (**1c**; 5.50 ppm), though *o*-acetylphenol is a weaker acid. More interestingly, in the spectrum of **1e**, not only the methine peak but all the peaks remarkably shifted upfield. This is due to the ring current effects in **1e**, where the protons of the IBVE unit are shielded by the two *o*-phenyl groups. This suggests that the polymer terminal would be sandwiched between the two phenyl rings, similarly to the growing ends in the metallocene-catalyzed olefin polymerization.

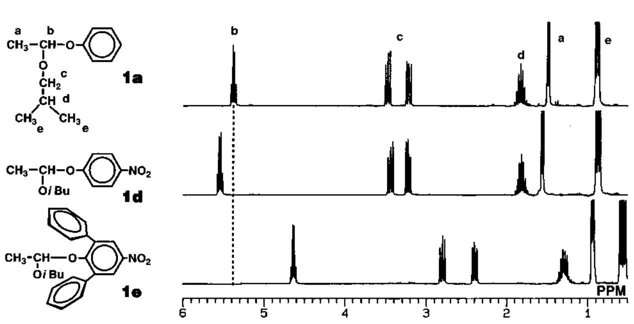


Figure 1. ^{1}H NMR spectra of aromatic acetals in CDCl$_3$ at 25 °C.

Table 1. Synthesis of Aromatic Acetals 1 from IBVE and Phenols

			synthesis conditions		
initiator (R)[a]	pK_a[b]	δ[H(b)],[c] ppm	method[a]	temp, °C	time, h
1a (H)	9.94	5.39	1	80	300
1b (CO$_2$Me)		5.44	1	80	50
1c (COMe)	7.84	5.50	1	80	40
1d (NO$_2$)	7.15	5.55	1	60	4
1e (NO$_2$)[d]		4.64	1	80	120
1f (COMe)[e]	10.82	5.54	2	−78	2

[a] See Scheme 2. [b] For precursor phenols; in water at 25 °C.[9] [c] ^{1}H NMR chemical shift of the methine proton (b) in **1**; see Figure 1. [d] R = 2,6-diphenyl-4-nitro. [e] *o*-Acetyl.

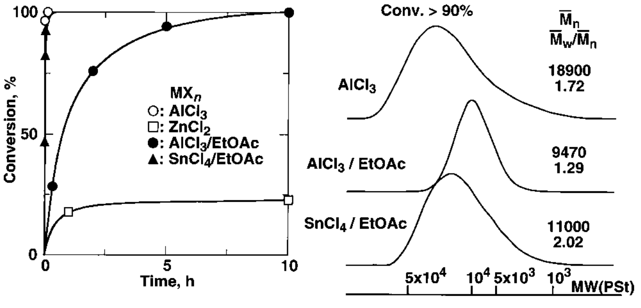


Figure 2. Polymerization of IBVE with **1c**/MX$_n$ in CH$_2$Cl$_2$ at 0 °C: [IBVE]$_0$ = 380 mM; [**1c**]$_0$ = 5.0 mM; [MX$_n$]$_0$ = 1.0 mM; EtOAc = 10 vol %.

2. Control of Cationic Polymerization with 1c. Cationic polymerization of IBVE with an aromatic acetal (**1c**) was investigated in conjunction with Lewis acids (MtX$_n$: AlCl$_3$, SnCl$_4$, ZnCl$_2$) in CH$_2$Cl$_2$ at 0 °C (Figure 2). The *p*-acetyl derivative **1c** alone did not polymerize IBVE, but the combination with AlCl$_3$ (or SnCl$_4$) led to a fast and quantitative polymerization (open circles). With ZnCl$_2$, a weaker Lewis acid, the reaction was very slow and stopped below 25% (open squares). The poly-

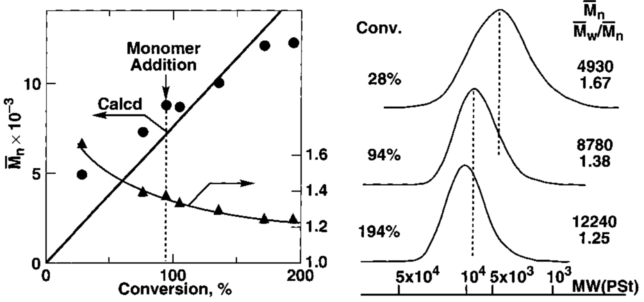


Figure 3. Monomer-addition experiment in the polymerization of IBVE with **1c**/$AlCl_3$ in CH_2Cl_2/EtOAc (8/1) at 0 °C: $[IBVE]_0 = [IBVE]_{add} = 380$ mM; $[\mathbf{1c}]_0 = 5.0$ mM; $[AlCl_3]_0 = 1.0$ mM. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **1c** molecule.

mers obtained with the **1c**/$AlCl_3$ system had broad MWDs and $\bar{M}_n$ higher than the calculated value assuming that one molecule of **1c** generates one living polymer chain. These results suggest a slow interconversion between the dormant and the activated species due to the less polarized acetal C−O terminal although the bond is weakly activated by an electron-withdrawing group, *p*-acetyl group, through the aromatic ring. This also led to slow initiation because the initiation occurs via the activated species generated by similar activation of the initiator or the dormant “unimer” terminal. For the same reason, a strong Lewis acid of $AlCl_3$ is needed to induce cationic polymerization by **1c**.

On the other hand, the addition of ethyl acetate (EtOAc; 10 vol %) to the **1c**/$AlCl_3$-initiated system retarded the polymerization (filled circles), and the $\bar{M}_n$ of the polymer became closer to the calculated value. This is probably due to the interaction with carbocationic species and/or the decrease of Lewis acidity by EtOAc, which decelerates propagation relative to initiation. Especially with $AlCl_3$, the $\bar{M}_n$ increased in direct proportion to the monomer conversion, and the MWD was relatively narrow ($\bar{M}_w/\bar{M}_n = 1.29$; conversion ∼ 100%). The **1c**/$AlCl_3$ initiating system is therefore effective for cationic polymerization of IBVE in the presence of EtOAc to give polymers with controlled molecular weights and narrow MWDs.

To investigate the long-lived nature of the IBVE polymerization with **1c**/$AlCl_3$ in CH_2Cl_2/EtOAc (8/1) at 0 °C, a fresh feed of monomer was added to the reaction mixture when the initial charge of monomer was almost consumed (94% conversion in 5 h). After the addition, the polymerization proceeded to reach an additional 94% conversion of the added IBVE in an additional 15 h. Figure 3 shows the $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of the polymers. After the monomer addition, the $\bar{M}_n$ continuously increased with monomer conversion, although the increase leveled off at the later stage, which probably resulted from chain transfer. The MWDs became narrower, and the peak of the MWD curves shifted to higher molecular weight region as the polymerization proceeded. Thus, the cationic polymerization of IBVE with the **1c**/$AlCl_3$ initiating system can be controlled in the presence of EtOAc.

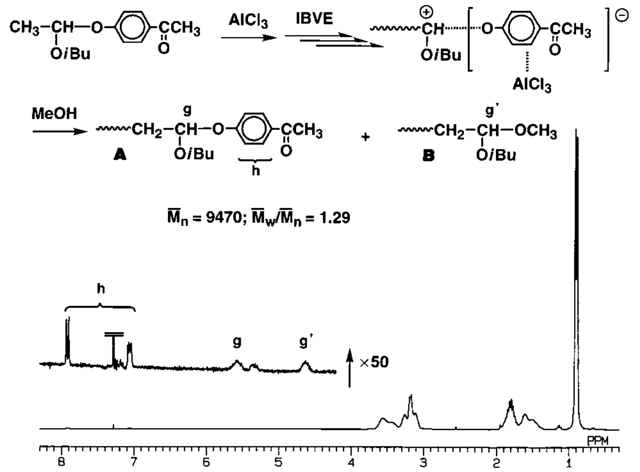


Figure 4. ^1H NMR spectrum of poly(IBVE) obtained with **1c**/$AlCl_3$ in CH_2Cl_2/EtOAc (8/1) at 0 °C.

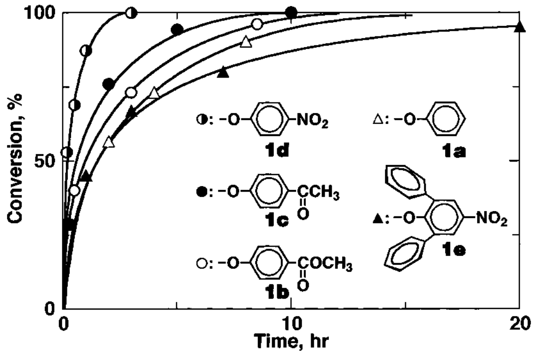


Figure 5. Time−conversion curves for polymerization of IBVE with **1**/$AlCl_3$ in CH_2Cl_2/EtOAc (8/1) at 0 °C: $[IBVE]_0 = 380$ mM; $[\mathbf{1}]_0 = 5.0$ mM; $[AlCl_3]_0 = 1.0$ mM.

3. End Group Analysis of the Polymers by ^1H NMR. The terminal structure of the polymers obtained with **1c** and $AlCl_3$ in CH_2Cl_2/EtOAc (9/1) was examined by ^1H NMR spectroscopy. Figure 4 shows the ^1H NMR spectrum of a typical sample obtained with **1c**/$AlCl_3$ after quenching the polymerization with methanol at 94% conversion, and the polymer was purified by preparative SEC ($\bar{M}_n = 9500$, $\bar{M}_w/\bar{M}_n = 1.29$). In addition to the signals at 0.8−3.7 ppm due to the IBVE repeat unit, a small broad peak g′ appeared at 4.6 ppm, assignable to the methine proton of the terminal acetal (B) that arises on the quenching with methanol. It is worth noting that the downfield signals h, characteristic of the aromatic protons of the 4-acetylphenoxy group, appeared along with the absorption g at 5.5 ppm, which is ascribed to the methine proton of the terminal aromatic acetal (A). These results show that there were two kinds of end groups, A (aromatic acetal) and B (nonaromatic acetal).

The existence of the terminal aromatic acetal confirms that the polymerization occurred from the aromatic acetal as an initiator, not by the exchange between the phenoxy anion and the chlorine in $AlCl_3$ followed by the activation of the resulting C−Cl bond by $AlCl_{3-n}(OAr)_n$ ($n = 1−3$). The fact that the concentration of $AlCl_3$ is lower than that of **1c** ($[\mathbf{1c}]_0/[AlCl_3]_0 = 5.0/1.0$ mM) also excludes the complete conversion of the C−OAr terminal into the C−Cl counterpart.

4. Effects of Ring Substituents in the Initiators. In addition to the *p*-acetyl derivatives (**1c**), other aromatic acetals (**1a**−**1e**) were employed for the polymerization of IBVE in conjunction with $AlCl_3$ in CH_2Cl_2/EtOAc (8/1). Irrespective of the substituents in **1**, polymerizations occurred smoothly and were completed in 3−20 h (Figure 5). The polymerization rate depended on the ring substituents, and except for the bulky derivative **1e**, the rate increased with the acidity of the corresponding phenols. This is in contrast to the fact

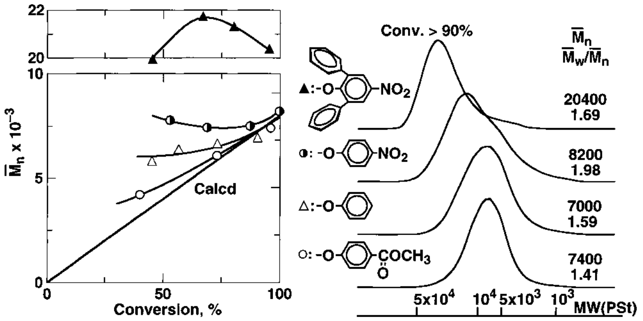


Figure 6. $\bar{M}_n$ and MWD curves of poly(IBVE) obtained with **1**/$AlCl_3$ in CH_2Cl_2/EtOAc (8/1) at 0 °C: $[IBVE]_0$ = 380 mM; $[\mathbf{1}]_0$ = 5.0 mM; $[AlCl_3]_0$ = 1.0 mM. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **1** molecule.

that for benzoates as initiators the rate was independent of the ring substituents.[5] These results suggest that the activation (dissociation) of the C−OAr bond should be assisted by the interaction between the activator (Lewis acid) and the ring substituents such as the acetyl group (Scheme 3).

Scheme 3

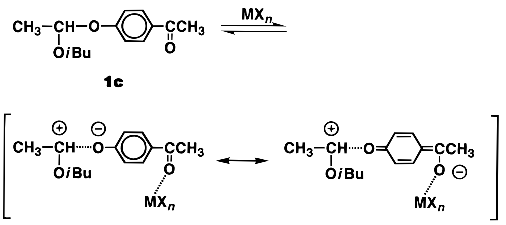


Figure 6 shows the $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of the polymers thus obtained with the aromatic acetals. As with **1c**, the $\bar{M}_n$ with the similar carbonyl version **1b** increased with the monomer conversion and was close to the calculated values. The MWDs were relatively narrow ($\bar{M}_w/\bar{M}_n \sim 1.4$). With **1a** and **1d**, the $\bar{M}_n$ values were higher than the calculated values in the early stages but became closer to them as the polymerization proceeded, probably because of the slower consumption of the initiators. On the other hand, the polymerization with **1e** gave much higher $\bar{M}_n$, suggesting that the sterically hindered 2,6-substituted structure prevented $AlCl_3$ from activating its C−O bond.

As described above (Scheme 1), the polymerizations with acetals **1** should involve an equilibrium between the dormant and the activated species. With the nitro derivative **1d**, the interconversion is slow as indicated by the higher $\bar{M}_n$ and the broader MWDs, although the polymerization is faster than that with **1b** and **1c**. This result suggests that the strongly electron-withdrawing *p*-nitro group enhances the generation of carbocations from **1d** but that the interaction between $AlCl_3$ and the carbonyl oxygen in **1b** and **1c** efficiently accelerates the interconversion between the dormant and the carbocationic species and results in the efficient consumption of the initiators.

Polymerizations in a less polar solvent (CCl_4) were also investigated with the **1**/$AlCl_3$ initiating systems in the presence of EtOAc. Polymerization proceeded much more slowly in CCl_4/EtOAc (8/1) than in CH_2Cl_2/EtOAc, and therefore a higher concentration of $AlCl_3$ was required ($[AlCl_3]_0$ = 10 mM). The $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of the polymers obtained therein are shown in Figure 7. The $\bar{M}_n$ of the polymer obtained with **1c**/$AlCl_3$ increased in direct proportion to monomer conversion, although the initiation efficiency stayed slightly lower than 1. The MWDs became narrower ($\bar{M}_w/\bar{M}_n$ = 1.14) than those in CH_2Cl_2. Even with **1e**/$AlCl_3$, the $\bar{M}_n$ of the polymer increased with the monomer conversion (open circles) and had relatively narrow MWDs ($\bar{M}_w/\bar{M}_n$ = 1.26). Most probably, propagation is slower in this less polar solvent which makes the MWDs narrower.

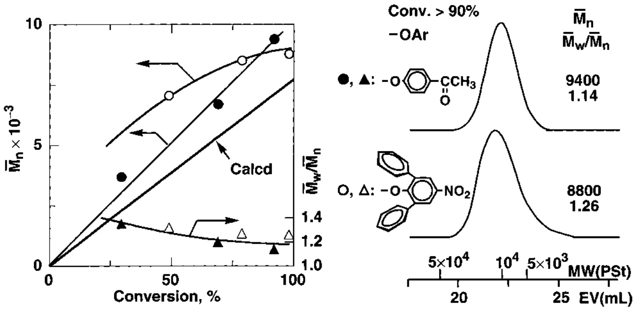


Figure 7. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(IBVE) obtained with **1**/$AlCl_3$ in CCl_4/EtOAc (8/1) at 0 °C: $[IBVE]_0$ = 380 mM; $[\mathbf{1}]_0$ = 5.0 mM; $[AlCl_3]_0$ = 10 mM. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **1** molecule.

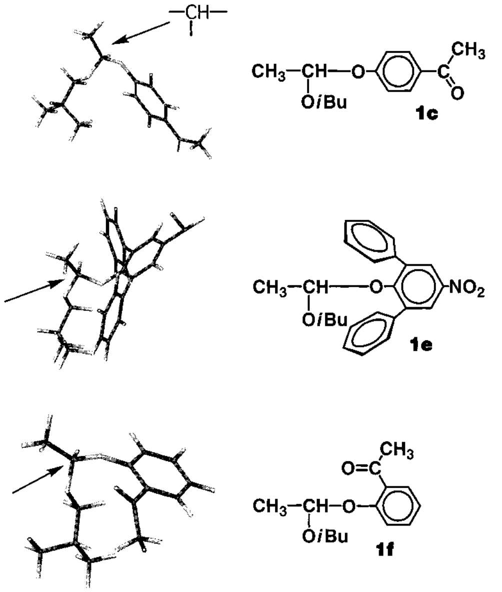


Figure 8. Computer-generated molecular models of the aromatic acetals (**1c**, **1e**, and **1f**).

5. Stereoregularity of Poly(IBVE). Figure 8 illustrates the computer-generated molecular models of some aromatic acetals (**1c**, **1e**, and **1f**). As expected from the ^1H NMR spectrum (Figure 1), the methine carbon (cation-generating site) in **1e**, similar to the dormant polymer terminal, is loosely sandwiched between the two *o*-phenyl rings. In **1f**, the *o*-carbonyl oxygen is close to the methine carbon, suggesting that, unlike the other acetals with para substituents, the counteranion from this *o*-carbonyl version may interact with the growing cation. Thus, these aromatic acetals afforded a unique environment around the cation-generating site, in contrast to the initiators with simple structures such as the adducts of hydrogen halides or carboxylic acids, which prompted us to investigate the possibility of a stereoregular polymerization.

The cationic polymerization of IBVE with these aromatic acetals was examined in toluene at −78 °C,

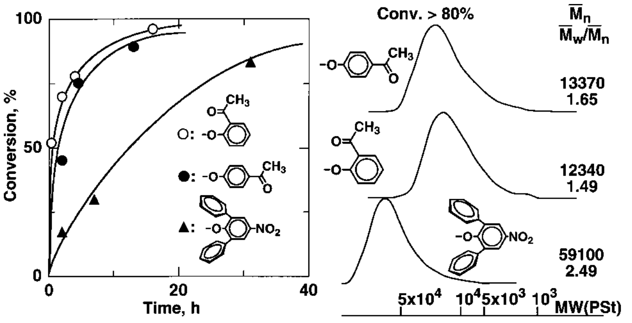


Figure 9. Polymerization of IBVE with **1**/$SnBr_4$ in toluene at −78 °C: $[IBVE]_0 = 380$ mM; $[\mathbf{1c}]_0 = 5.0$ mM; $[SnBr_4]_0 = 10$ mM.

Table 2. Meso Dyad Contents of Poly(IBVE) Obtained with 1/MX_n[a]

	initiator			
MX_n (Lewis acid)	**1c**	**1e**	**1f**	IBVE−HCl[d]
$SnBr_4$[b]	79	78	81	79
$SnCl_4$[b]	77	79	81	74
$AlCl_3$[c]	52	54		

[a] $[M]_0/[\mathbf{1}]_0 = 380/5.0$ mM. [b] $[MX_n]_0 = 10$ mM in toluene at −78 °C. [c] $[MX_n]_0 = 1.0$ mM in CH_2Cl_2 at 0 °C. [d] The HCl adduct of IBVE: $CH_3CHCl(OiBu)$.

because low temperatures and less polar solvents usually increase isotacticity. As Lewis acids, $SnCl_4$ and $SnBr_4$ were also employed, which have higher solubility than $AlCl_3$ in toluene at −78 °C. The polymerization proceeded smoothly and quantitatively (Figure 9). The $\overline{M}_n$ of the polymers were higher than the calculated values probably due to the slow initiation with $SnBr_4$.

Table 2 summarizes the meso dyad contents of poly(IBVE) thus obtained. Meso dyads were determined from the signals of main-chain methylene carbons of poly(IBVE) in ^{13}C NMR spectra. The polymers with $AlCl_3$ in CH_2Cl_2 at 0 °C were almost atactic, despite their controlled molecular weights and MWDs. In the polymerization at −78 °C, meso contents were higher with the aromatic acetals than with hydrogen chloride as initiators. Irrespective of Lewis acids, **1f** from *o*-acetylphenol gave the highest meso contents. In particular, with $SnCl_4$ the meso values clearly increased with steric hindrance around the cationic site (or counteranions: **1f** > **1e** > **1c** > HCl). This point should be further investigated.

Experimental Section

Materials. The phenol derivatives were obtained commercially and used without further purification: *p*-$CH_3OC(O)$ (Tokyo Kasei; purity > 99.0%), *p*-$CH_3C(O)$ (Tokyo Kasei; purity > 98.0%), *o*-$CH_3C(O)$ (Tokyo Kasei; purity > 98.0%), *p*-NO_2 (Tokyo Kasei; purity > 99.0%), 4-NO_2-2,6-di-C_6H_5 (Aldlich; purity > 99.0%), unsubstituted (Wako Chemicals; purity > 98.0%). The IBVE−HCl adduct was prepared as reported.[12]

Commercial IBVE (Tokyo Kasei; purity > 99%) was washed with 10% aqueous sodium hydroxide solution and then water, dried overnight over potassium hydroxide, and distilled twice over calcium hydride before use. $AlCl_3$ (Aldrich; purity > 99.99%), $SnBr_4$ (Aldrich; purity > 99%), and $SnCl_4$ (Aldrich; purity > 99%) were used as received. CH_2Cl_2 and CCl_4 as solvents were dried overnight over calcium chloride and doubly distilled over phosphorus pentoxide and then over calcium hydride before use. Toluene as a solvent and *n*-hexane as an internal standard for gas chromatography were dried overnight over calcium chloride and doubly distilled over calcium hydride before use. EtOAc was doubly distilled over calcium hydride before use.

Syntheses of Aromatic Acetals. As described above, there were two methods of synthesizing aromatic acetals **1** (see Scheme 1 and Table 1).

(a) Method 1. The phenol derivatives were mixed with IBVE (molar ratio: phenol derivative/IBVE = 1/2) under dry nitrogen and heated to 60−80 °C for 4−300 h. Then, the reaction mixture was washed with 10% aqueous sodium hydroxide solution and water to remove a small amount of unreacted phenols and evaporated to remove unreacted IBVE in excess. The remaining liquid or solid was distilled under reduced pressure (**1a**), recrystallized from *n*-hexane (**1d** and **1e**), or freeze-dried with benzene (**1b** and **1c**), respectively, and then the adducts **1** were isolated. The purity was over 99% by ^1H NMR.

(b) Method 2. To a solution of 1.5 mL of *o*-acetylphenol in 4.7 mL of dry toluene was added dropwise at −78 °C 7.2 mL of 1.7 M *n*-pentane solution of *tert*-butyllithium under dry nitrogen, and stirring was continued for 1 h. A 1.0 M *n*-hexane solution of the IBVE−HCl adduct was added dropwise, and the mixture was kept stirred for 30 min at −78 °C and then over 1.5 h at room temperature. The mixture was washed with 10% aqueous sodium hydroxide solution and then water and evaporated to dryness. The residue was freeze-dried with benzene to give the adduct **1f** quantitatively (yield = 98%, purity > 99%).

Polymerization Procedures. The polymerizations were carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for IBVE polymerization is given below. The polymerization was initiated by adding solutions of $AlCl_3$ (0.5 mL) in EtOAc into a mixture (4.5 mL) of IBVE (0.25 mL) and *n*-hexane (0.25 mL) containing the aromatic acetal **1** in CH_2Cl_2 at 0 °C. The total volume of the reaction mixture was thus 5.0 mL. The polymerization was terminated with prechilled methanol (2.0 mL). Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with *n*-hexane as an internal standard. The quenched reaction mixture was washed with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to give the polymer.

Measurements. The MWD, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$ ratios of the polymers were measured by size-exclusion chromatography (SEC) in chloroform at room temperature on three polystyrene gel columns (Shodex K-802 + K-803 + K-804) that were connected to a Jasco Trirotar-V precision pump and a Jasco 830-RI refractive index detector. The columns were calibrated against 11 standard poly(styrene) samples (Polymer Laboratories; $\overline{M}_n = 630−220\,000$; $\overline{M}_w/\overline{M}_n = 1.06−1.22$) as well as monomer. ^1H NMR spectra were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-GSX270 spectrometer, operating at 270.7 MHz, and ^{13}C NMR spectra were done at 55 °C and 67.9 MHz. Polymers for ^1H and ^{13}C NMR analysis were fractionated by preparative SEC (column: Shodex K-2002).

Computer-Generated Molecular Models of 1. Molecular mechanics calculations (MM2) were carried out using the CAChe system (CAChe Scientific) to optimize the spatial structures of **1**. MM2 parameters were used as force field parameters, and optimization was done by the conjugate gradient method until the convergence energy became less than 4.18 J/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 between −180° and 120° in five steps and for all the double bonds between −180° and 90° in three steps), followed by selecting 10 conformers with the local lowest energies and by further optimization of them.

References and Notes

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