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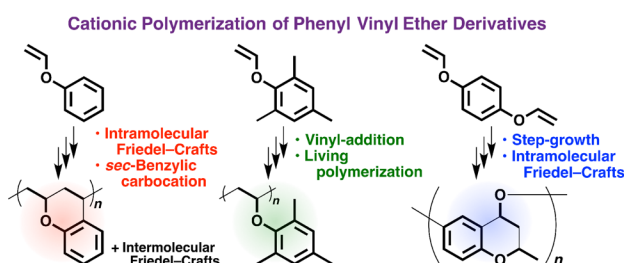
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Cationic Polymerization of Phenyl Vinyl Ethers: Investigations of the Propagation Mechanism, the Living Polymerization of *o*-Substituted Derivatives, and the Step-Growth Polymerization of Divinyl Derivatives

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Abstract

The cationic polymerization of phenyl vinyl ether (PhVE) was investigated to elucidate the reason why it is much more difficult to obtain high-molecular-weight polymers of PhVE than with alkyl vinyl ethers. The detailed analysis of the products by NMR spectroscopy indicated that the propagation proceeded not via a sequential vinyl-addition reaction but via an intramolecular Friedel–Crafts reaction between a PhVE-derived carbocation and the phenyl ring of the penultimate unit and subsequent generation of another carbocation via the cleavage of the *sec*-benzylic ether moiety of the resulting chromane-type structure. The intermolecular Friedel–Crafts reaction also likely occurred in the polymerization conducted in dichloromethane. The introduction of electron-withdrawing substituents into the phenyl ring of PhVE did not suppress the intramolecular Friedel–Crafts reactions, whereas the blocking of the *o*-positions of the ring by methyl substitution resulted in propagation by the vinyl-addition reactions. In particular, the cationic polymerization of

2,4,6-trimethylphenyl vinyl ether proceeded in a living manner under the optimized conditions. In addition, the copolymerization of PhVE with *p*-methoxybenzaldehyde occurred via vinyl- and carbonyl-addition reactions without Friedel-Crafts reactions, resulting in a polymer with an alternating sequence. Moreover, such a Friedel–Crafts reaction was successfully employed as a bond-forming reaction for the synthesis of polymers from 1,4-divinyloxybenzene via a step-growth mechanism.

Introduction

Aromatic rings can dramatically influence polymerizations mediated by cationic reactive species either beneficially or detrimentally. The reaction of a carbocationic intermediate with an aromatic ring serves as the bond-forming reaction in the synthesis of phenolic resins, including phenol–formaldehyde resins and polybenzoxazines.^{1–3} Styrene derivatives can undergo cationic polymerization due to the resonance effect of the aromatic ring attached to the vinyl group, and this resonance effect stabilizes the generated carbocation. However, the intramolecular Friedel–Crafts reaction of the styrene derivative-derived carbocation with the aromatic ring in the penultimate unit results in indanyl ring formation accompanied by the liberation of a proton, which induces a chain transfer reaction.^{4–6} A Friedel–Crafts reaction can also occur between the styrene derivative-derived carbocation and an aromatic ring of another chain. Such intermolecular reactions can be employed for synthesizing branched polymers, such as star-shaped and graft polymers,^{7–8} unlike the detrimental intramolecular reaction. The Friedel–Crafts reaction of an isobutylene-derived propagating carbocation with low-molecular-weight (low-MW) aromatic compounds, such as furan,⁹ pyrrole derivatives,^{10,11} and alkoxybenzenes,¹² is an effective method for preparing end-functionalized polyisobutylenes.

Phenyl vinyl ether (PhVE; Chart 1) derivatives, which are synthesized from phenol derivatives, are potentially polymerizable through a cationic mechanism similar to that of alkyl vinyl ethers (VEs). However, several studies conducted in the 1950–70s^{13–16} showed that high-MW polymers could not be obtained by the cationic polymerization of PhVE. Imoto and coworkers suggested that some side reactions, such as the liberation of phenol and acid-catalyzed

rearrangement of PhVE to an *o*-vinylphenol, occurred during the polymerization.¹³ The intramolecular Friedel–Crafts reaction of the PhVE-derived carbocation with the phenyl group in the penultimate unit was also suggested, although experimental evidence was not presented. Okamura and coworkers suggested that the polymerization proceeded via a vinyl-addition reaction but resulted in oligomers due to frequent, unidentified chain transfer reactions.^{14,15} In addition, they concluded that PhVE is more reactive than styrene based on the results of the cationic copolymerization. Kruglova and coworkers suggested that the polymerization proceeded via both the vinyl-addition reaction and a Friedel–Crafts reaction between the PhVE-derived carbocation and the *p*-position of the phenyl ring of a PhVE monomer.¹⁶ They also suggested the occurrence of the intramolecular Friedel–Crafts reaction that was suggested by Imoto and coworkers. However, the cationic polymerization of PhVE needs to be investigated in more detail because the mechanisms suggested in past studies are not well supported partly due to the lack of high-resolution spectroscopic analysis.

In this study, we examined the cationic polymerization of PhVE to elucidate the propagation mechanisms. Based on our investigation of the polymerization products (oligomers) by NMR spectroscopy, we suggest a different mechanism than those suggested in past studies. Specifically, intramolecular Friedel–Craft reactions and subsequent carbocation generation via the cleavage of the *sec*-benzylic ether moiety of the resulting chromane-type structure were most likely responsible for the propagation of the PhVE polymerization. To suppress such reactions, PhVE derivatives with various substituents on the aromatic ring (Chart 1) were prepared and subjected to this polymerization. Blocking the *o*- or *o,p*-positions with methyl groups successfully led to vinyl-addition propagation reactions. In addition, we examined the alternating copolymerization of PhVE with an aromatic aldehyde. Moreover, an intramolecular Friedel–Craft reactions was employed for the synthesis of a polymer from 1,4-divinyloxybenzene (DVOB) via a step-growth mechanism.

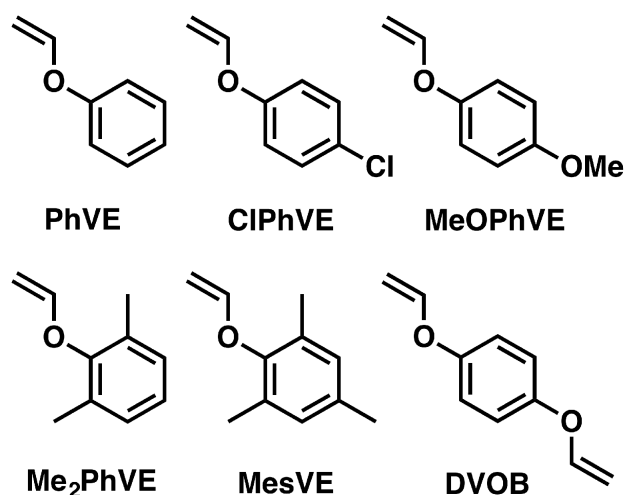


Chart 1. PhVE and its derivatives examined in this study.

Experimental Section

Materials. PhVE and its derivatives were synthesized by the E2 reaction of the corresponding 2-haloethyl aryl ethers or the reaction of vinyl acetate and the corresponding phenol derivative.^{17,18} Some 2-haloethyl aryl ethers were synthesized by the reaction of the corresponding phenol derivatives and 1,2-haloethane.¹⁹ The details of the syntheses are described in the Supporting Information. The adduct of isobutyl VE with HCl (IBVE–HCl) and 2,4,4-trimethylpentyl chloride (TMPCl) were prepared by the addition reaction of isobutyl VE or 2,4,4-trimethyl-1-pentene with HCl, respectively, according to the reported methods.^{20,21} (1-Chloroethyl)benzene (St–HCl; TCI, >97.0%) was distilled twice over calcium hydride under reduced pressure. Ethanesulfonic acid (Sigma-Aldrich, 95%) was used as received. Commercially available SnCl₄ (Sigma-Aldrich, 1.0 M solution in heptane), EtAlCl₂ (Wako, 1.0 M solution in hexane), and TiCl₄ (Sigma-Aldrich, 1.0 M solution in toluene) were used without further purification. Stock solutions of FeCl₃ in diethyl ether and GaCl₃ in hexane were prepared from FeCl₃ (Sigma-Aldrich, 99.99%) and GaCl₃ (Sigma-Aldrich, >99.999%), respectively. 2-Chloroethyl VE (CEVE; TCI, >97.0%) was washed with a 10% aqueous sodium hydroxide solution and then distilled twice over calcium hydride under reduced pressure. *p*-Methylstyrene (pMeSt; TCI, >96.0%) and *p*-chlorostyrene (pClSt; TCI, >98%) were washed with a 10% aqueous sodium hydroxide solution, dried overnight over sodium sulfate, and distilled twice over calcium hydride under reduced pressure. 2-Methyl-1-pentene (TCI,

>98.0%) and heptane (Nacalai-Tesque, 99%) were distilled twice over calcium hydride. (–)- β -Pinene (Sigma-Aldrich, >99.0%) and *p*-methoxybenzaldehyde (pMeOBzA; Nacalai-Tesque, 99%) were distilled twice over calcium hydride under reduced pressure. 1,4-Dioxane (Wako, 99.5%) was distilled over calcium hydride and then lithium aluminum hydride. Toluene (Wako, >99.5%) and dichloromethane (Wako, super dehydrated) were dried by passage through a solvent purification column (Glass Contour).

Polymerization procedures. The following is a typical polymerization procedure. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki, PJ-206A; the air temperature was approximately 450 °C) under dry nitrogen. Toluene, heptane, PhVE, and IBVE–HCl solution in toluene were sequentially added into the tube using dry syringes. The polymerization was started by the addition of a prechilled solution of SnCl₄ in toluene to the monomer solution at 0 °C. After a predetermined time, the reaction was terminated by the addition of methanol containing a small amount of aqueous ammonia. The quenched mixture was diluted with dichloromethane and then washed with hydrochloric acid, aqueous sodium hydroxide solution, and water. The volatiles were then removed under reduced pressure to yield the product. The monomer conversion was determined by gas chromatography (column packing material: PEG-20M-Uniport HP; GL Sciences Inc.) using heptane as an internal standard.

Characterization. The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C with polystyrene gel columns [TSKgel GMH_{HR}-M $\times$ 2 (exclusion limit MW = 4×10^6 ; bead size = 5 μ m; column size = 7.8 mm id $\times$ 300 mm); flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive-index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from the chromatograms with respect to 16 polystyrene standards (Tosoh; MW = 5.0×10^2 to 1.09×10^6 , $M_w/M_n < 1.2$). The absolute M_n values were determined with a GPC system comprising of a Viscotek VE 1122 pump, polystyrene gel columns (TSKgel GMH_{HR}-M $\times$ 2; flow rate = 0.7 mL/min; eluent: tetrahydrofuran), and a Viscotek TDA 305 triple detector [refractive index, laser light scattering (λ = 670 nm; 90 ° RALS and 7 ° LALS), and differential pressure viscometer]. The separation of the polymerization products by preparative GPC

was conducted in chloroform at room temperature with a polystyrene gel column [TSKgel G3000H_{HR} (exclusion limit MW = 6×10^4 ; bead size = 5 μm ; column size = 21.5 mm id $\times$ 300 mm); flow rate = 2.0 mL/min] connected to a JASCO PU-2086 Plus pump, a JASCO UV-2075 ultraviolet detector, and a Tosoh RI-8020 refractive-index detector. A JASCO RV-2080-02 recycle valve unit was also used for precise fractionation by recycle GPC. The NMR spectra were recorded using a JEOL JNM-ECA 500 spectrometer (500.16 MHz for ^1H and 125.77 MHz for ^{13}C) in chloroform-*d* at 30 °C. The thermal properties of the polymers were examined with a Shimadzu DSC-60 Plus differential scanning calorimeter.

Results and Discussion

Cationic Polymerization of Phenyl Vinyl Ether: Elucidation of the Reaction Mechanisms by Structural Analysis

The cationic polymerization of PhVE was examined under various conditions suitable for the cationic polymerization of alkyl VEs.^{22–27} PhVE was consumed in the reactions using several metal chlorides as Lewis acid catalysts in conjunction with IBVE–HCl as the cationogen in toluene at 0 °C; however, the products were not high-MW polymers and instead were low-MW oligomers with M_n of $0.2\text{--}0.4 \times 10^3$ (entries 1, 6, 8, and 10 in Table 1; Figure S1),²⁸ as in the cases of past studies. The use of ethyl acetate, which is an effective Lewis basic additive for the living polymerization of alkyl VEs, had negligible effects on the MWs (entry 2; Figure 1A, left).

Table 1. Cationic Polymerization of PhVE in toluene.^a

Entry	Lewis Acid	Solvent	Temp (°C)	Time	Conv. (%) ^b	$M_n \times 10^{-3}$ ^c	M_w/M_n ^c
1	SnCl ₄	toluene	0	4 h	60	0.3	1.36
				8 h	97	0.3	1.43
2 ^d	SnCl ₄	toluene	0	6 h	75	0.2	1.13
3	SnCl ₄	CH ₂ Cl ₂	0	3 min	60	0.3	1.51
				10 min	100	0.5	2.18
				1 h	100	0.9	4.33
4	SnCl ₄	CH ₂ Cl ₂	−78	29 h	100	0.6	2.45
5 ^e	SnCl ₄	hexane	0	2 h	1	0.3	1.60
6	EtAlCl ₂	toluene	0	10 min	26	0.3	1.99
7	TiCl ₄	toluene	0	1 h	0	—	—

8	FeCl ₃	toluene	0	2 min	51	0.2	1.14
9 ^f	FeCl ₃	toluene	-78	24 h	60	0.2	1.11
10	GaCl ₃	toluene	0	10 s	100	0.4	5.15

^a [PhVE]₀ = 0.60 (entries 1, 3, and 6–10) or 0.65 (entries 2, 4 and 5) M, [IBVE–HCl]₀ = 4.0 mM (except for entries 5 and 9), [Lewis acid]₀ = 4.0 (entries 1, 3 and 6–10) or 10 (entries 2, 4 and 5) mM. See Figures 1 and S1 for MWD curves. ^b Determined by gas chromatography. ^c Determined by GPC (polystyrene standards). ^d [Ethyl acetate] = 50 mM. ^e A cationogen was not used. ^f As the cationogen, EtSO₃H (4.0 mM) was used instead of IBVE–HCl.

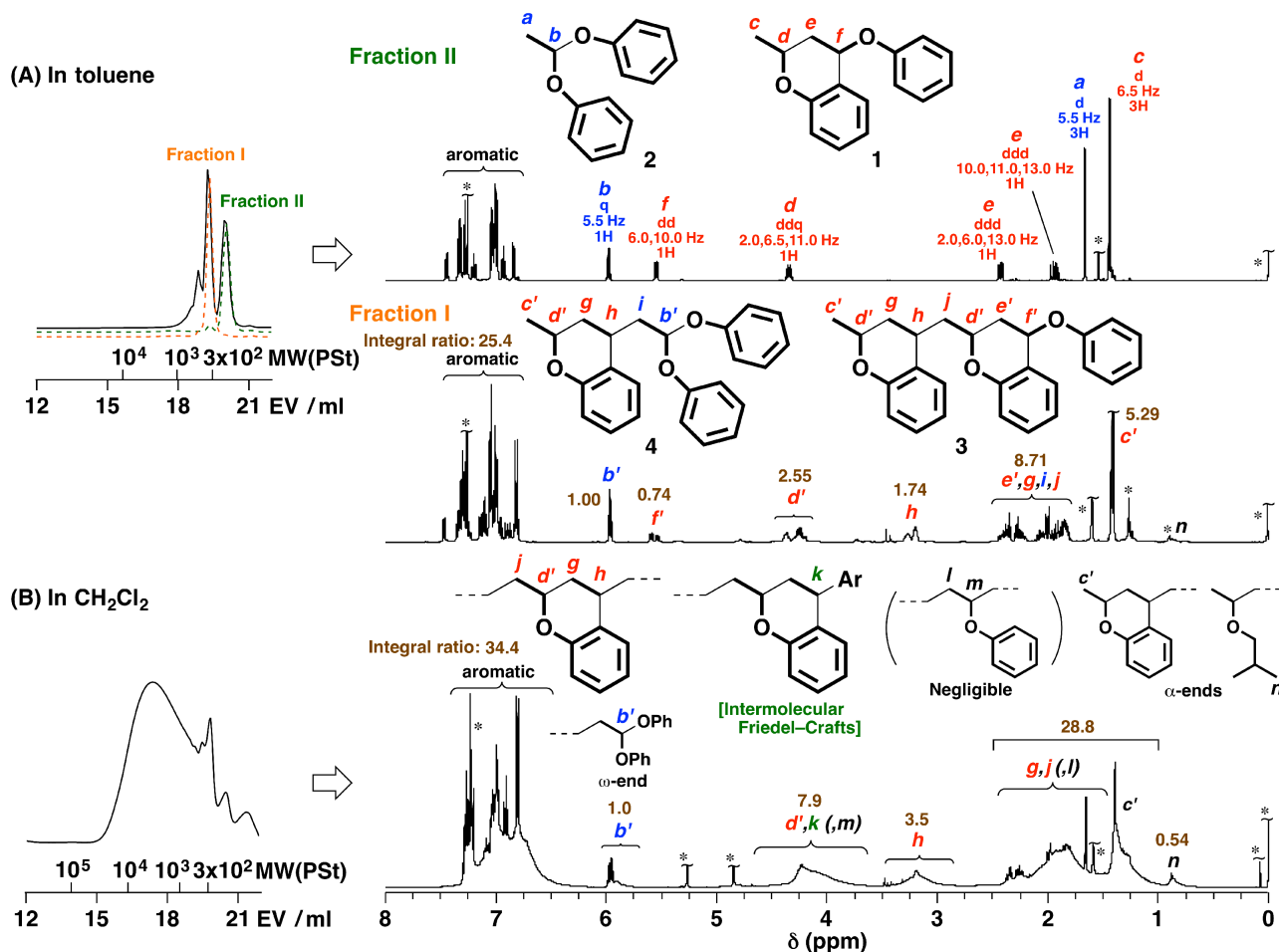
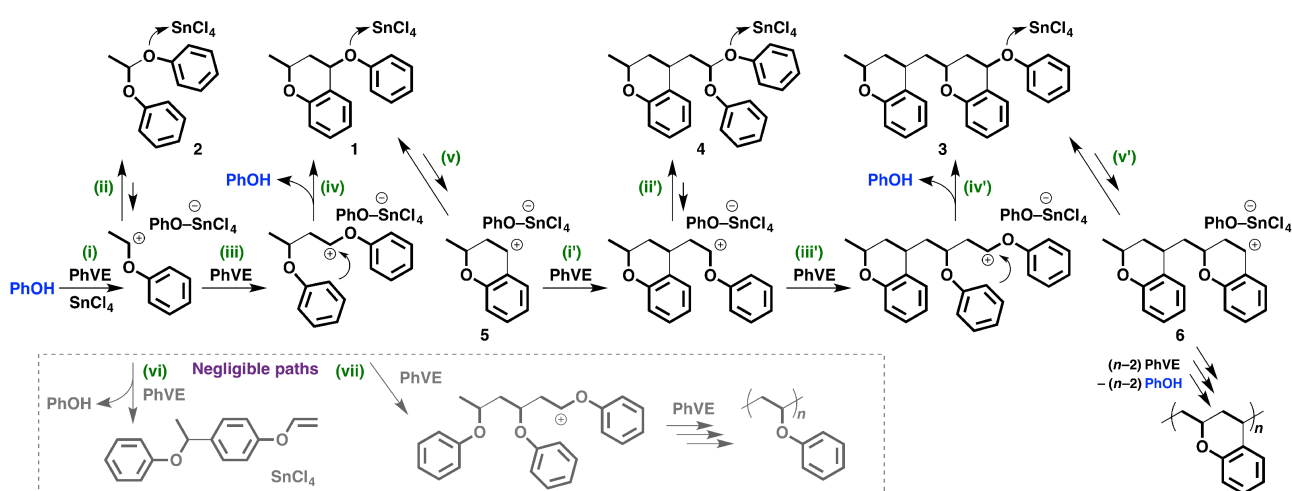


Figure 1. MWD curves (solid curve: the original products, broken curve: fractions separated by preparative GPC) and ¹H NMR spectra of the products obtained by the polymerization of PhVE in (A) toluene (entry 2 in Table 1) or (B) dichloromethane (entry 3; 1 h) (see the footnote of Table 1 for the reaction conditions; see Figure S2 for larger spectra). * Water, TMS, grease, vaseline, CHCl₃, phenol, and dichloromethane.

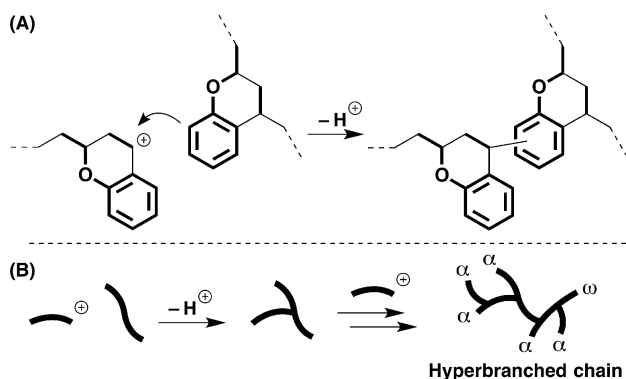
The reaction of PhVE in toluene most likely proceeded via an intramolecular Friedel–Crafts reaction at the propagating chain end and the abstraction of a phenoxy group, which was

determined based on structural analysis by ^1H NMR spectroscopy. The product obtained with SnCl_4 in toluene (entry 2) was analyzed after fractionation by preparative GPC (Figure 1A). The spectrum of the lower-MW fraction (fraction II; green curve) had peaks assignable to two compounds **1** and **2**. Product **1** is a chromane-type compound with a *sec*-benzylic ether moiety (peaks c, d, e, and f). The product was most likely produced by an intramolecular Friedel–Crafts reaction of a carbocation consisting of two PhVE units (path iv). This reaction is accompanied by the liberation of phenol. The other product **2** in fraction II, which is an acetal with two phenoxy groups (peaks a and b), was generated through the reaction with a phenol (paths i in Scheme 1). Moreover, the phenoxy group of the *sec*-benzylic ether moiety in the chromane-type compound **1** can be abstracted by the Lewis acid catalyst (path v), which is followed by the reaction with a PhVE monomer (path i'). Subsequently, the generated carbocation **5** reacts with the abstracted phenoxy group (path ii') or reacts with a PhVE and then undergoes another intramolecular Friedel–Crafts reaction (paths iii' and iv'), which results in oligomers **4** or **3** with an acetal end or a *sec*-benzylic ether end, respectively. Indeed, the higher-MW fraction (fraction I; orange curve) was composed mostly of these two compounds, as confirmed by ^1H NMR analysis (Figure 1A). In addition, the ESI-MS spectrum of the product had signals with m/z values that correspond to the above structures (Figure S3). Friedel–Crafts reactions between the carbocations and toluene, which was used as a solvent, did not occur because the electron-density of the aromatic ring of toluene is lower than that of the alkoxy-attached aromatic ring derived from PhVE.



Scheme 1. Mechanisms of the cationic polymerization of PhVE. Reactions that are not shown here, such as the initiation from a cationogen, also occur.

The reaction of PhVE in dichloromethane yielded a product with a higher MW (entry 3 in Table 1) than that obtained in toluene (entries 1 and 2). More interestingly, the MW increased even after the complete consumption of PhVE (Figure S1B). Given that the polymerization proceeds via the mechanism explained above (Scheme 1), a polymer consisting of chromane-type repeating units will be obtained, and the MW will not increase after all the PhVE monomers are consumed. In such a case, in the ^1H NMR spectrum of the product (see Figures S4–S7 for ^{13}C and 2D NMR spectra of the product obtained in dichloromethane at $-78\text{ }^\circ\text{C}$), the two peaks assignable to the methine groups attached to an oxygen (3.7–4.3 ppm; peak d' in Figure 1B) and to an aryl ring (2.8–3.4 ppm; peak h) will have comparable integrals. However, the former peak was obviously larger than the latter. These results most likely suggest that the intermolecular Friedel–Crafts reaction between the chromane-type carbocation and the aryl ring of another chain occurred (Scheme 2A). A methine group attached to two aryl rings was generated by this reaction, and it exhibited a peak at approximately 4 ppm, which is responsible for the peak in this region being larger than the peak at 2.8–3.4 ppm in the ^1H NMR spectrum. Furthermore, the intermolecular Friedel–Crafts reaction can occur even after the complete consumption of PhVE, resulting in the formation of hyperbranched chains, which explains the higher MWs of the products (Scheme 2B). In addition, a peak assigned to the *sec*-benzylic ether end (peak f' in Figure 1A) was difficult to detect in the ^1H NMR spectrum of the product obtained in dichloromethane at a longer reaction time (Figure 1B), while a peak of the acetal end (peak b') was detected. The former end was likely completely consumed by the intermolecular Friedel–Crafts reaction because the styrene-type carbocation derived from the *sec*-benzylic ether structure is more reactive than the VE-type carbocation derived from the acetal structure. The high activity of the cationic polymerization in dichloromethane, which is a more polar solvent than toluene, is probably responsible for the occurrence of the intermolecular Friedel–Crafts reaction because the polar solvent favors the generation of carbocations via the cleavage of *sec*-benzylic ether moieties. The reaction in toluene using GaCl_3 , which exhibits a high catalytic activity, also resulted in a product containing a high-MW fraction, possibly for a similar reason. In addition, the reaction in hexane, which is a less polar solvent than toluene, resulted in products similar to those obtained in toluene (entry 5 in Table 1; Figure S8).



Scheme 2. (A) Intermolecular Friedel–Crafts reaction and (B) a schematic illustration of the reactions and a typical polymer chain obtained by the polymerization of PhVE in dichloromethane.

The reaction mechanisms demonstrated above are different from those suggested in previous studies.^{13–16} Specifically, propagation by a Friedel–Crafts reaction between a PhVE-derived carbocation and the *p*-position of a PhVE monomer (path vi in Scheme 1) and the sequential vinyl-addition reactions of PhVE monomers (path vii) are most likely negligible, which is supported by various results, such as the absence of peaks assignable to vinyl protons and the presence of a peak assignable to the aryl-adjacent methine at approximately 3 ppm in the 1H NMR spectra. In addition, a chromane ring was suggested to only be generated at the chain end in a previous study;^{13,16} however, chromane ring formation was demonstrated to occur continuously during propagation in this study.

Polymerization of PhVE Derivatives with a Chloro or Methoxy Group at the *p*-Position on the Aromatic Ring: The Effect of Electron-Withdrawing Substituents

To suppress the Friedel–Crafts reactions and promote vinyl-addition reactions, chloro and methoxy groups were introduced onto the aromatic ring at the *p*-position of PhVE. These groups are inductively electron withdrawing; hence, the intramolecular Friedel–Crafts reactions were expected to be suppressed due to the decrease in the electron density at position *meta* to the electron-withdrawing group. However, the polymerizations of 4-chlorophenyl VE (ClPhVE) and 4-methoxyphenyl VE (MeOPhVE) yielded products similar to those obtained from the reaction of

PhVE. The products had very low MWs (Figure 2), and peaks assignable to structures resulting from the intramolecular Friedel–Crafts reactions and the abstraction of phenoxy groups were detected in the ^1H NMR spectra (Figure S9). The results indicate that the electron-withdrawing effects of these groups were insufficient to suppress the Friedel–Crafts reactions.

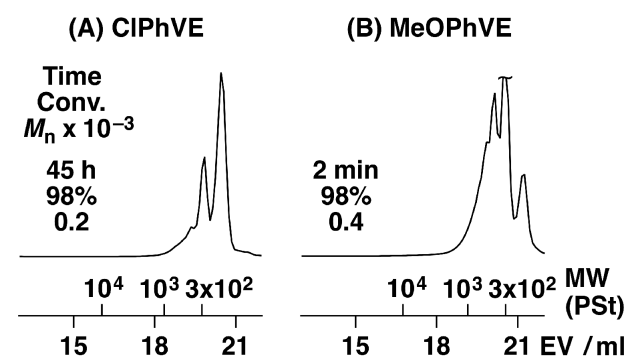
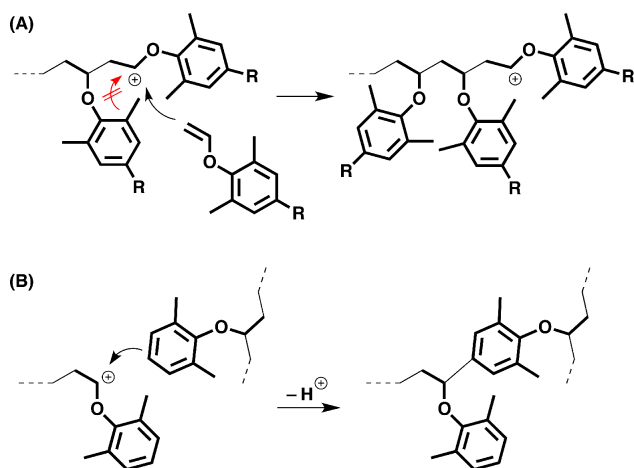


Figure 2. MWD curves of the products obtained by the polymerization of (A) ClPhVE and (B) MeOPhVE ($[\text{ClPhVE}]_0 = 0.61$ M or $[\text{MeOPhVE}]_0 = 0.27$ M, $[\text{IBVE-HCl}]_0 = 4.0$ mM, $[\text{SnCl}_4]_0 = 4.0$ mM, in toluene at 0°C).

Polymerization of PhVE Derivatives with Methyl Groups at the *o*- or *o,p*-Positions on the Aromatic Ring: The Blocking of the Friedel–Crafts Reactions

A PhVE derivative with two methyl groups at the *o*-positions of the aromatic ring (2,6-dimethylphenyl VE; Me_2PhVE) was designed for the purpose of blocking the intramolecular Friedel–Crafts reactions (Scheme 3A). The monomer was synthesized by the E2 reaction of 2,6-dimethylphenoxy-2-bromoethane, which was prepared from 2,6-dimethylphenol and 1,2-dibromoethane. The cationic polymerization of Me_2PhVE was conducted using SnCl_4 or GaCl_3 as a catalyst in conjunction with IBVE–HCl as a cationogen at 0°C (entries 1 and 2 in Table 2). A polymer with an M_n of 6.5×10^3 was obtained when GaCl_3 was used as a catalyst in dichloromethane. Importantly, analysis of the product by ^1H and ^{13}C NMR spectroscopy (Figures S11 and S12) suggested that the polymerization of Me_2PhVE proceeded via vinyl-addition reactions. Intramolecular Friedel–Crafts reactions appeared to be suppressed via the blocking of the *o*-positions with methyl groups.



Scheme 3. (A) The suppression of the intramolecular Friedel–Crafts reaction by the introduction of methyl groups at the *o*-positions of the aromatic ring [R = H (Me₂PhVE) or Me (MesVE)] and (B) the intermolecular Friedel–Crafts reaction of the propagating carbocation to the *p*-position of the pendant aromatic ring of poly(Me₂PhVE).

Table 2. Cationic Polymerization of Me₂PhVE^a

entry	Lewis acid	solvent	temp (°C)	time	conv. (%)	$M_n \times 10^{-3}$	M_w/M_n
1	SnCl ₄	toluene	0	45 h	44	0.6	1.75
2	GaCl ₃	CH ₂ Cl ₂	0	3 min	85	6.5	2.02
3	GaCl ₃	CH ₂ Cl ₂	−78	195 min	94	14.2	1.63
4	GaCl ₃	toluene	−78	50 h	96	12.7	1.16

^a [Me₂PhVE]₀ = 0.59 (entry 1) or 0.42 (entries 2–4) M, [IBVE–HCl]₀ = 4.0 mM, [Lewis acid]₀ = 4.0 mM. See Figure S10 for the MWD curves.

To control the MWs and MWDs in the polymerization of Me₂PhVE, appropriate reaction conditions using GaCl₃ as a catalyst were examined. Polymerization at −78 °C resulted in a product with a higher MW than that obtained at 0 °C (entry 3 in Table 2), and the MWD was still relatively broad. The use of toluene instead of dichloromethane as the solvent provided better control of the polymerization (entry 4). The MWD was obviously narrower than that in dichloromethane. Therefore, the polymerization under the optimized conditions was examined in more detail. The monomer conversion smoothly increased with reaction time, and the first-order plot was linear (Figure 3A), which indicates that termination reactions did not occur in the polymerization. Moreover, the M_n values of the products increased linearly with an increase in monomer conversion, suggesting that the occurrence of transfer reactions was negligible. Peaks assignable to structures

derived from side reactions, such as β -proton elimination, were not detected by ^1H NMR analysis (Figure 4A). However, a small shoulder peak appeared in the MWD curve of the product obtained in the latter stage of the polymerization. The MW of the shoulder peak was approximately twice that of a main peak. This suggests that the intermolecular Friedel–Crafts reaction between the propagating chain and the *p*-position of the aromatic ring in another polymer chain most likely occurred in the polymerization (Scheme 3B).

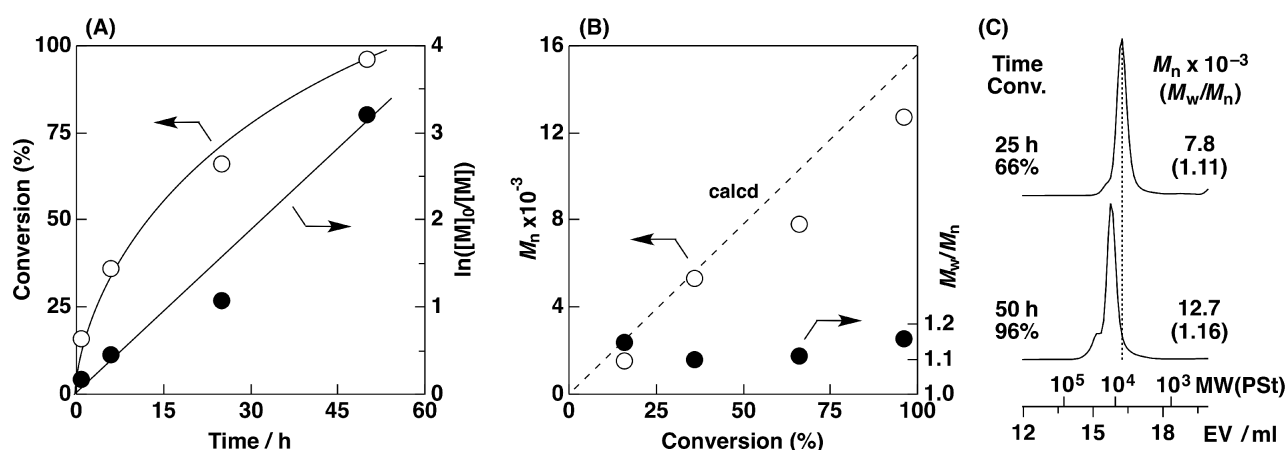


Figure 3. (A) Time–conversion (open) and $\ln([M]_0/[M])$ –conversion (filled) plots of the polymerization of Me_2PhVE , (B) M_n (open) and M_w/M_n (filled) values, and (C) MWD curves of the obtained polymers ($[\text{Me}_2\text{PhVE}]_0 = 0.42 \text{ M}$, $[\text{IBVE-HCl}]_0 = 4.0 \text{ mM}$, $[\text{GaCl}_3]_0 = 4.0 \text{ mM}$, in toluene at -78°C).

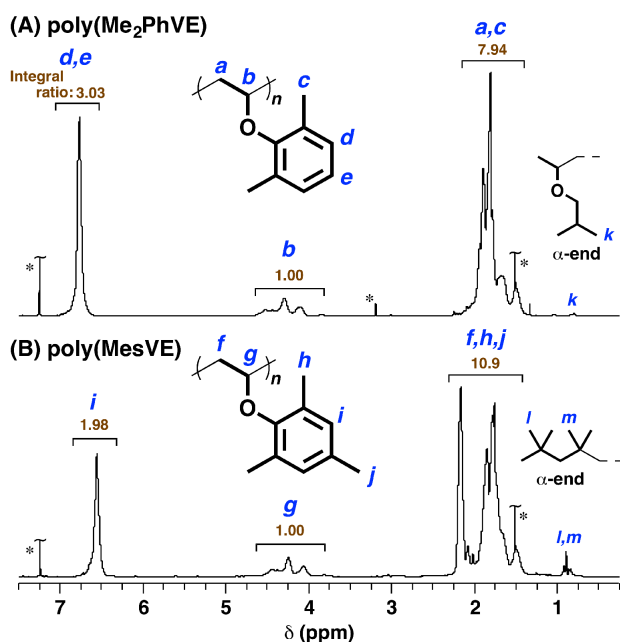


Figure 4. ^1H NMR spectra of (A) poly(Me_2PhVE) (Figure 3C, lower) and (B) poly(MesVE) (Figure 5C, lower). See Figure S13 for larger spectra. * Water, methanol, and CHCl_3 .

To suppress the intermolecular Friedel–Crafts reaction and achieve living polymerization, an additional methyl group was introduced at the *p*-position of the aromatic ring of the monomer. The polymerization of 2,4,6-trimethylphenyl VE (mesityl VE; MesVE), which was synthesized by a process similar to that of Me_2PhVE , was conducted under conditions similar to those used for the polymerization of Me_2PhVE .²⁹ As shown in Figure 5A, the polymerization smoothly proceeded and reached over 90% conversion. The obtained products had unimodal and narrow MWDs (Figure 5C). Moreover, the M_n values increased linearly with increasing monomer conversion (Figure 5B). Importantly, the MWs determined by GPC with a light-scattering detector (red open circles in Figure 5B) were larger than those determined by GPC with polystyrene calibration (black open circles) and were close to the theoretical values based on the amounts of monomer and cationogen. ^1H NMR analysis suggested that the polymerization proceeded via vinyl-addition reactions, and structures resulting from side reactions were absent (Figure 4B). In addition, the MW calculated from the integral ratios of the peaks of the methine protons in the main chain (peak *g*) and the cationogen fragment (peaks *l* and *m*) was 10.4×10^3 , which was comparable to the value by GPC with a light-scattering detector (10.0×10^3). The results indicate that the polymerization of MesVE proceeded in a living manner. Long-lived species were also generated in the polymerizations when using SnCl_4 , EtAlCl_2 , or TiCl_4 as a catalyst (Figure S15); however, the reaction was more controlled when using GaCl_3 .

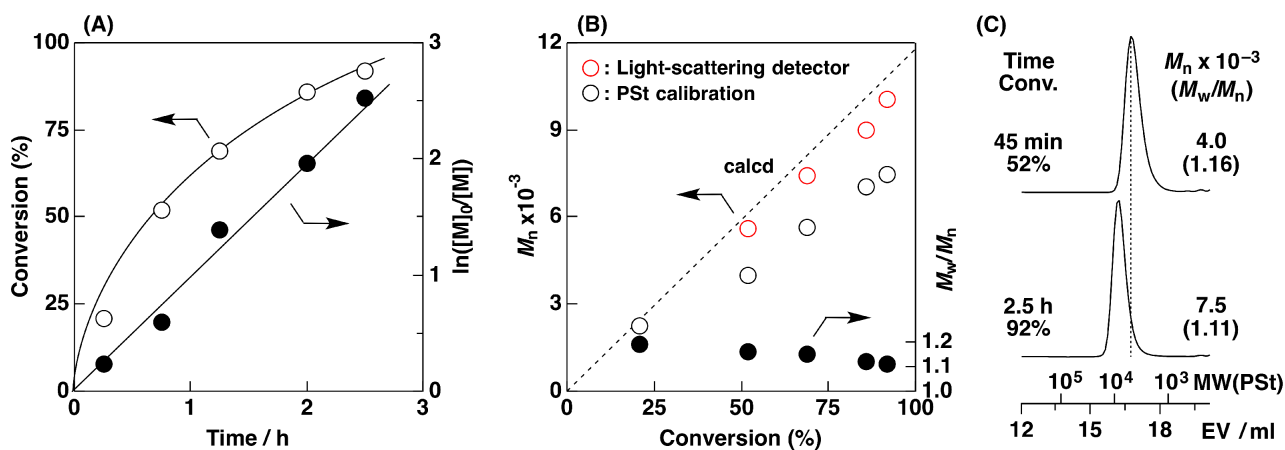


Figure 5. (A) Time–conversion (open) and $\ln([M]_0/[M])$ –conversion (filled) plots of the polymerization of MesVE, (B) M_n (open) and M_w/M_n (filled) values, and (C) MWD curves of the obtained polymers ($[\text{MesVE}]_0 = 0.29 \text{ M}$, $[\text{TMPCl}]_0 = 4.0 \text{ mM}$, $[\text{GaCl}_3]_0 = 8.0 \text{ mM}$, in toluene at -78°C).

The livingness of the polymerization was also confirmed by the monomer-addition experiment (Figure 6). A fresh supply of MesVE was added into the reaction solution when the monomer conversion reached approximately 90%. The fresh monomer was then consumed, and the MWD of the product shifted to a higher-MW region without residual peaks, which suggests that the living polymerization of MesVE proceeded using GaCl_3 as a catalyst in toluene at -78°C .³⁰

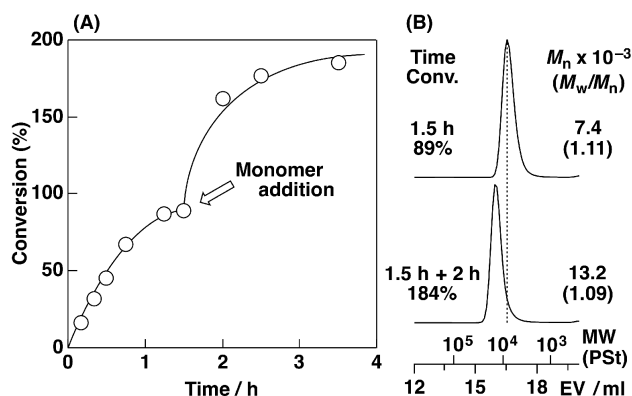


Figure 6. Monomer-addition experiment of the polymerization of MesVE: (A) Time–conversion plots and (B) MWD curves of the obtained polymers ($[\text{MesVE}]_0 = 0.29 \text{ M}$, $[\text{MesVE}]_{\text{added}} = 0.29 \text{ M}$, $[\text{TMPCl}]_0 = 4.0 \text{ mM}$, $[\text{GaCl}_3]_0 = 8.0 \text{ mM}$, in toluene at -78°C).

The reactivity of MesVE as a cationically polymerizable monomer was evaluated through the copolymerization with VE and styrene-derived monomers (Table S1). In the copolymerizations of MesVE with CEVE or pMeSt, MesVE was hardly consumed, and homopolymers of the comonomers were almost obtained, indicating that MesVE is less reactive than these monomers. In contrast, pClSt, which is a less reactive monomer than pMeSt, was not polymerized in the copolymerization with MesVE. Only a small amount of MesVE (13%) was consumed, resulting in an oligomer. In addition, neither MesVE nor comonomers were consumed in the copolymerizations with 2-methyl-1-pentene or β -pinene. The inertness of these monomers in copolymerizations is

probably because the ether moiety of the MesVE monomer functioned as a Lewis base and suppressed the activity of the Lewis acid catalysts, as in the case of ethyl acetate suppressing isobutene polymerization.³¹

The thermal properties of poly(PhVE derivative)s were examined by DSC analysis (Figure 7). Poly(Me₂PhVE) and poly(MesVE) exhibited T_g s of 85 and 100 °C, respectively. The T_g s are higher than those of typical alkyl VE polymers owing to the aromatic rings. In particular, the T_g of poly(MesVE) is comparable to those of poly(methyl methacrylate) (105 °C) and polystyrene (100 °C);³² hence, poly(PhVE derivative)s can be a promising candidate as a new hard segment.

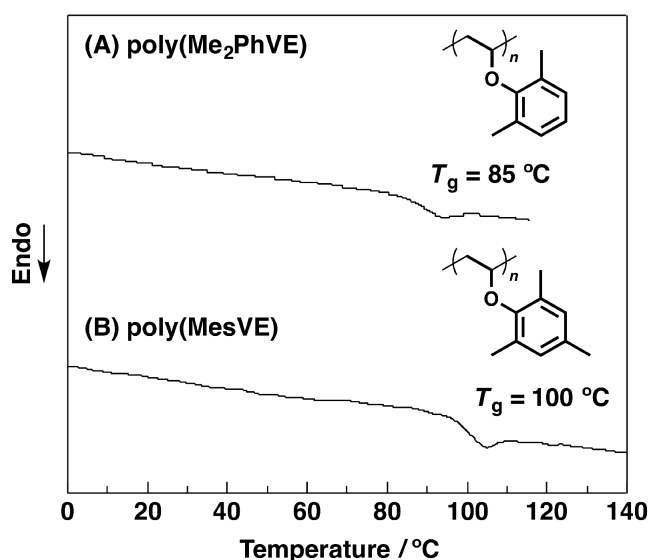


Figure 7. DSC thermograms of (A) poly(Me₂PhVE) (obtained under the same conditions as those for entry 3 in Table 2; $M_n(\text{GPC}) = 10.8 \times 10^3$) and (B) poly(MesVE) (Figure 5C, lower) (2nd heating scan; heating rate: 10 °C/min).

Cationic Alternating Copolymerization of PhVE and Aromatic Aldehyde

As another way to suppress intramolecular Friedel–Crafts reactions of PhVE, we examined the cationic copolymerization with aromatic aldehydes. We have developed a controlled cationic alternating copolymerization of alkyl VEs and aromatic aldehydes.^{33,34} Alternating copolymers are produced when an aromatic aldehyde that exhibits sufficiently higher reactivity than a VE is used because aromatic aldehydes do not undergo homopolymerization due to their very low

ceiling temperature. Therefore, the intramolecular Friedel–Crafts reaction between the PhVE-derived carbocation and the phenoxy group of the penultimate unit will not occur because the homopropagation of PhVE was completely suppressed by the preferential crossover to an aldehyde monomer.

The copolymerization of PhVE and pMeOBzA was conducted in toluene at $-78\text{ }^{\circ}\text{C}$ using the $\text{EtSO}_3\text{H}/\text{GaCl}_3/1,4\text{-dioxane}$ initiating system, which was demonstrated to be an effective system for the controlled alternating copolymerization of alkyl VE and aromatic aldehydes in our previous studies.^{33,34} Comparable amounts of PhVE and pMeOBzA were consumed in the copolymerization, and a polymer with an M_n of 3.1×10^3 was obtained (Figure 8; black solid curve). A cyclic trimer consisting of one PhVE and two pMeOBzA units was also generated as a side product in a manner similar to the copolymerization of alkyl VE and aromatic aldehyde (a peak with an asterisk in Figure 8). The ^1H NMR spectrum (Figure 9A) of the polymer fraction separated by preparative GPC (broken curve in Figure 8) showed peaks assignable to the acetal and *sec*-benzylic moieties resulting from the crossover from PhVE to pMeOBzA and from pMeOBzA to PhVE, respectively, at 4.1–5.5 ppm. Comparing the integrals of these peaks to other peaks, we can conclude that the aldehyde content in the product was approximately 50% and that the product has an alternating sequence. In addition, acid hydrolysis of the product yielded *p*-methoxycinnamaldehyde (Figure 9B), as in the case of the degradation of the alternating copolymers of alkyl VEs and aromatic aldehydes, which supported that the original polymer was an alternating copolymer. The alternating copolymer (a sample that was produced under similar conditions to those in Figure 8; $M_n(\text{GPC}) = 5.8 \times 10^3$ [the high-MW portion separated by preparative GPC]) exhibited a T_g of $39\text{ }^{\circ}\text{C}$ (Figure S17).

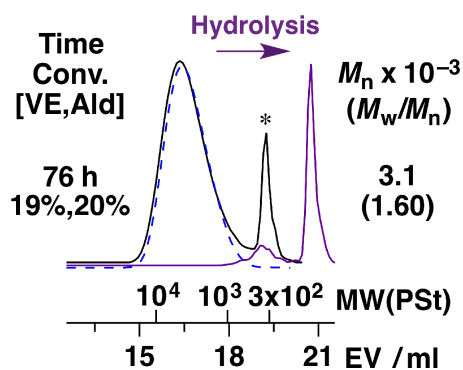


Figure 8. MWD curves of the product obtained by the copolymerization of PhVE and pMeOBzA (solid, black; * cyclic trimer consisting of one PhVE and two pMeOBzA units), the polymer after purification by preparative GPC (dotted, blue), and acid hydrolysis product (solid, purple; hydrolysis was conducted with 0.5 M HCl(aq) in 1,2-dimethoxyethane at room temperature for 2 h (polymer: 0.5 wt%); hydrolyzed after purification by preparative GPC) ([PhVE]₀ = 0.60 M, [pMeOBzA]₀ = 0.60 M, [EtSO₃H]₀ = 4.0 mM, [GaCl₃]₀ = 4.0 mM, [1,4-dioxane]₀ = 1.0 M in toluene at −78 °C). The M_n and M_w/M_n were calculated from the polymer peak.

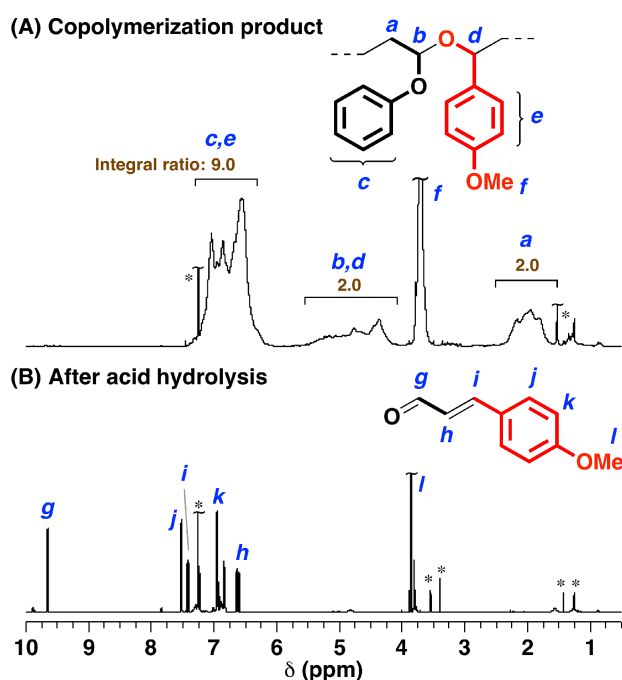
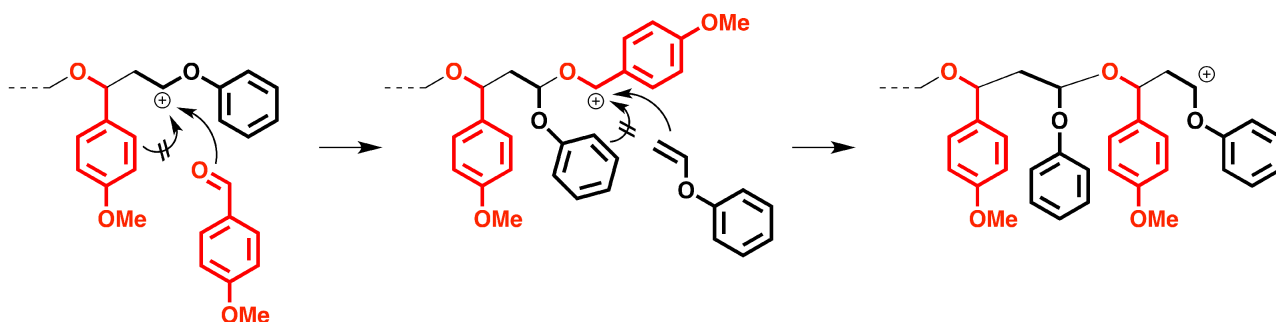


Figure 9. ¹H NMR spectra of (A) the copolymer of PhVE and pMeOBzA (after purification by preparative GPC; dotted curve in Figure 8) and (B) acid hydrolysis product (solid, purple curve in Figure 8). See the caption of Figure 8 for the polymerization conditions. See Figure S16 for larger spectra. * Water, CHCl₃, vaseline, and 1,2-dimethoxyethane.

The alternating propagation was successful likely for the following reasons. The PhVE-derived carbocation with a penultimate pMeOBzA unit (Scheme 4, left) does not undergo an intramolecular Friedel–Craft reaction because the *o*-position of the *p*-methoxyphenyl ring in the pMeOBzA unit by the alkyl group is less activated than the *o*-position of the phenyl ring of the PhVE unit by the alkoxy group. The high reactivity (nucleophilicity) of the pMeOBzA monomer in

the reaction with the PhVE-derived carbocation is also responsible for the suppression of the intramolecular Friedel–Craft reaction. The pMeOBzA-derived carbocation with a penultimate PhVE unit (Scheme 4, middle) does not react with the phenyl ring of the PhVE unit because the carbocation is less reactive than the PhVE-derived carbocation due to the resonance effects of the adjacent alkoxy and *p*-methoxyphenyl moieties. The instability of the five-membered cyclic acetal structure that would be generated by the intramolecular Friedel–Crafts reaction may also be responsible for the inertness.

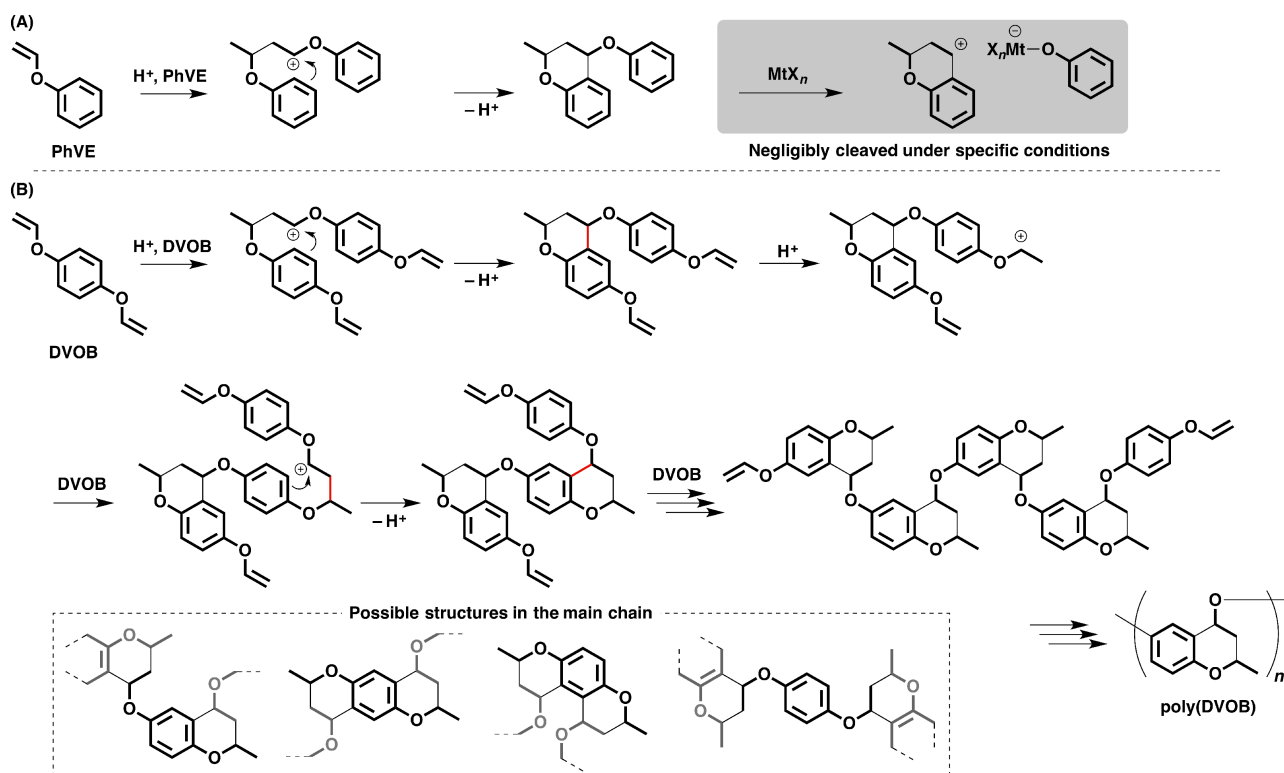


Scheme 4. Crossover reactions from the PhVE-derived carbocation to pMeOBzA and from the pMeOBzA-derived carbocation to PhVE.

Cationic Polymerization of 1,4-Divinyloxybenzene via a Friedel–Crafts-Type Step-Growth Mechanism

The formation of the chromane-type structure is an undesired reaction in terms of obtaining high-MW polymers in the polymerization of PhVE; however, this reaction can be regarded as promising for the synthesis of a new type of polymer. Specifically, divinylxybenzenes can potentially be polymerized via a step-growth mechanism, as shown in Scheme 5B. The polymerization of 1,4-diisopropenylbenzene was reported to proceed in a similar manner via indanyl ring formation.^{35,36} However, unlike the case of 1,4-diisopropenylbenzene, the cleavage of the *sec*-benzylic ether moiety by a Lewis acid catalyst, which occurred in the polymerization of PhVE (Scheme 5A), potentially occurs as a side reaction in the polymerization of divinylxybenzenes. Therefore, reaction conditions that are suitable for the formation of chromane-type structures but unsuitable for *sec*-benzylic ether cleavage are required for the

successful polymerization of divinylbenzenes. Interestingly, the use of FeCl_3 as a catalyst appears to fit these requirements (entry 8 in Table 1). An investigation of the reaction of PhVE under various conditions using FeCl_3 showed that the selectivity was improved by using EtSO_3H in toluene at -78°C (entry 9; Figure S1G; Figure 10C).



Scheme 5. (A) The reaction of PhVE and (B) the polymerization mechanism of DVOB.

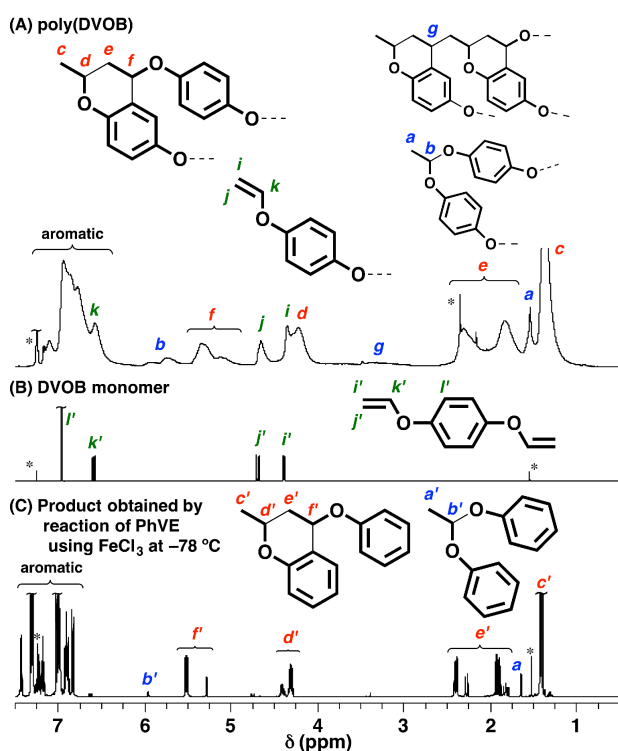


Figure 10. ^1H NMR spectra of (A) the product obtained by the polymerization of DVOB (Figure 11A, lower; after purification by reprecipitation from methanol), (B) DVOB monomer, and (C) the product obtained by the reaction of PhVE using FeCl_3 (entry 9 in Table 1). See Figure S18 for larger spectra. * Water and CHCl_3 .

Based on the devised strategy with the appropriate conditions, the polymerization of DVOB was conducted using FeCl_3 in toluene at $-78\text{ }^\circ\text{C}$. The reaction did not generate an insoluble fraction, which indicates that the crosslinking reactions that are typical in polymerizations of divinyl monomers did not occur (Figure 11A). Analysis of the product by ^1H , ^{13}C , and 2D NMR spectroscopy (Figures 10A, and S19–S22) indicated that the polymerization proceeded via the formation of chromane-type structures (Scheme 5B), although a small number of structures resulting from the cleavage of the *sec*-benzylic ether moiety were detected (peak g in Figure 10A). Further investigations of more appropriate conditions and monomer structures to control the polymerization of DVOB and its derivatives are in progress. In addition, the bond-forming reactions potentially occur via several modes such as “head-to-head”, “head-to-tail”, and “tail-to-tail” modes, resulting in di-, tri-, and tetrasubstituted aryl rings, as shown in the square in Figure 5B. Moreover, tetrasubstitution can occur at 1,2,4,5- and 1,2,3,4-positions. Therefore, the obtained polymer has a complicated main chain. Some analytical methods are required to determine the detailed structures.

In contrast to the reaction using FeCl_3 , insoluble products were obtained when GaCl_3 was used as the catalyst (Figure 11B), which is most likely because the *sec*-benzylic ether moieties were cleaved and the generated carbocations participated in crosslinking reactions. The high activity of GaCl_3 in the cleavage of the *sec*-benzylic ether moieties corresponds to the generation of the high-MW fraction in the reaction of PhVE (entry 10 in Table 1; Figure S1H). A higher oxophilicity of GaCl_3 than FeCl_3 may be responsible for the difference between the reactions using these Lewis acids.

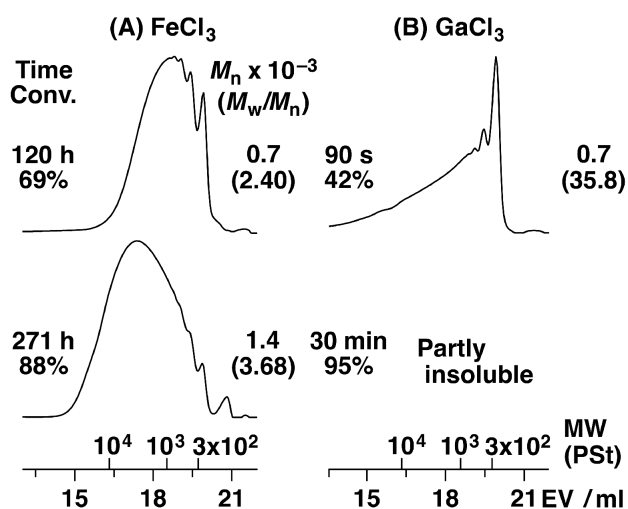


Figure 11. MWD curves of the products obtained by the polymerization of DVOB using (A) FeCl_3 and (B) GaCl_3 ($[\text{DVOB}]_0 = 0.30 \text{ M}$, $[\text{EtSO}_3\text{H}]_0 = 4.0 \text{ mM}$, $[\text{FeCl}_3]_0 = 10 \text{ mM}$ or $[\text{GaCl}_3]_0 = 4.0 \text{ mM}$, in toluene at -78°C).

Conclusion

In conclusion, the cationic polymerization of PhVE was demonstrated to proceed not by a vinyl-addition mechanism but by chromane-type structure formation via an intramolecular Friedel–Crafts reaction and subsequent generation of a carbocation via cleavage of the *sec*-benzylic ether moiety. The intermolecular Friedel–Crafts reaction also operated in dichloromethane, which led to an increase in the MWs after complete consumption of PhVE. An attempt to suppress the intramolecular Friedel–Crafts reaction by introducing electron-withdrawing groups onto the phenyl ring of PhVE was unsuccessful; however, the blocking of the *o*-positions by methyl substitution was effective, resulting in cationic polymerization by vinyl-addition propagation reactions.

Moreover, the living polymerization of MesVE proceeded under the optimized conditions, yielding polymers with predictable MWs and narrow MWDs. The copolymerization of PhVE with pMeOBzA was also effective for suppressing Friedel–Crafts reactions and yielded acid-degradable alternating copolymers with acetal moieties in the main chain. In addition, the intramolecular Friedel–Crafts reaction, which prevented the generation of high-MW polymers in the case of PhVE, was usefully employed as a bond-forming reaction in the polymerization of the divinyl monomer. The chemistry demonstrated in this study will further our understanding and utilization of aromatic ring-containing cationic reactions for the synthesis of various types of polymer materials.

Associated Content

Supporting Information

Synthetic methods of PhVE and its derivatives, polymerization data, and NMR and ESI-MS spectra of polymerization products.

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Notes

The authors declare no competing financial interest.

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28. The conversion of PhVE in the reaction using TiCl_4 was 0% (entry 7). However, the reaction using a larger amount of TiCl_4 (10 mM) in dichloromethane in a longer time (6 h) resulted in PhVE conversion of 100% ($M_n = 0.3 \times 10^3$, $M_w/M_n = 2.19$).
29. TMPCl was used as a cationogen instead of IBVE–HCl because the former was slightly superior to the latter in terms of the reaction rate (Figure S14). St–HCl also functioned as an effective cationogen.
30. The highest M_n (polystyrene calibration) of the poly(MesVE) that we have ever obtained is 34.7×10^3 . Higher MWs will also be achievable at larger $[\text{monomer}]_0/[\text{cationogen}]_0$ ratios although influence of impurities, such as adventitious water, will become non-negligible.
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