The Synthesis and Polymerization of Phenylvinylxyboranes*

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ABSTRACT: Phenyldivinylxyborane, $\text{PhB}(\text{OCH}=\text{CH}_2)_2$ (DVOB), and chlorophenylvinylxyborane, $\text{PhB}(\text{OCH}=\text{CH}_2)\text{Cl}$ (VOBCl), were synthesized by the reaction of phenyl-dichloroborane and mercuridiacetaldehyde. Diphenylvinylxyborane (VOB) and di-*n*-butylvinylxyborane were not isolated from the reaction mixture because of their rapid spontaneous polymerization.

DVOB was polymerized by radical and cationic initiators. Poly(DVOB) polymerized with radical initiators was found to have a perfectly cyclized structure with exclusively six-membered rings. On the other hand, cationically polymerized polymers were highly crosslinked, indicating incomplete cyclization. The radical poly(DVOB) was converted into poly(vinyl alcohol) by hydrolysis, the tacticity of which was found to be slightly isotactic.

VOBCl was also polymerized by radical initiators, yielding polymers which had structures similar to the radical poly(DVOB), indicating the occurrence of a cyclization and elimination reaction during the polymerization. VOBCl was not polymerized by cationic initiators.

VOB was polymerized spontaneously and was ascertained to have been polymerized by a radical mechanism.

KEY WORDS Phenylvinylxyboranes / Vinylxyboranes / Radical Polymerization / Cyclopolymerization / Cationic Polymerization / Stereoregularity / Poly(vinyl alcohol) / B—O conjugation /

A number of vinylxymetal compounds have been reported for metals such as aluminum,¹ titanium,² sodium,³ lithium,³ potassium,³ iron,³ magnesium,³ silicon,⁴ germanium,^{5,6} and tin.⁷ These vinylxy compounds may be regarded as a new class of vinyl monomers, but there have been few studies of their polymerizability.

The polymerization behaviors have been studied for the vinylxy compounds of carbon,⁸ silicon,^{8,9} and germanium.⁶ With these analogues, the rate of radical homopolymerization was found to increase with increasing number of vinylxy groups for a particular element and in the order of $\text{C} < \text{Si} < \text{Ge}$ with the same number of vinylxy groups.¹⁰ The compounds having more than two vinylxy groups were cyclopolymerized to some extent, yielding five-membered rings in addition to six-membered rings.

α - and/or β -substituted vinylxyboranes have been reported as reaction intermediates in the reactions of alkylboranes or alkylthioboranes with carbonyl compounds or α,β -unsaturated carbonyl compounds.¹¹ However, unsubstituted vinylxyborane compounds, which are regarded as either vinyl esters of boric acid or homologues of vinyl ether, have not been reported. In this paper, studies about the preparation and polymerization of phenyldivinylxyborane, chlorophenylvinylxyborane, diphenylvinylxyborane, and di-*n*-butylvinylxyborane are described.

RESULTS AND DISCUSSION

Polymerization of Phenyldivinylxyborane (DVOB)

DVOB was polymerized either by radical initiators or thermally, as shown in Table I. Although the monomer was susceptible to hydrolysis by atmospheric moisture, poly(DVOB) was found to be unchanged after being exposed to the atmosphere for one month at room tem-

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perature. These radical polymers, even the polymers obtained at high conversions, were completely soluble in benzene, toluene, pyridine, acetone, tetrahydrofuran, chloroform, and methylene chloride and insoluble in aliphatic hydrocarbons, methanol, and water.

The IR spectrum of poly(DVOB) is shown in Figure 1, together with that of DVOB. The polymers show no vinyl group absorption at 1645, 950, or 875 cm^{-1} . The absorption of $\nu_{\text{O-H}}$ is very small, excluding the possibility that the

vinyl groups are lost by hydrolysis. The NMR spectra of poly(DVOB) also showed no signal of vinyl protons. Thus, a complete cyclopolymerization may be concluded for this case.

These polymers were readily converted into PVA by hydrolysis with an aqueous alkaline solution. Some properties of PVA derived from poly(DVOB) are summarized in Table II. The yields of PVA from poly(DVOB) were much more than those calculated on the basis of the polymerization of one vinyl group per molecule. This fact qualitatively confirms the cyclopolymerization. The 1,2-glycol contents of the derived PVA were very small, even less than that of a commercial PVA. This fact shows that the cyclization reaction yielded six-membered rings exclusively.

Divinyl monomers may cyclopolymerize, but the cyclization usually does not take place completely and uniformly. For example, divinyl compounds of silicon and germanium are known to cyclopolymerize incompletely to give polymers having residual pendant vinyl groups. A considerable number of five-membered rings are formed in addition to six-membered rings.^{6,9} DVOB is a particular unconjugated divinyl monomer, which is completely cyclopolymerized to six-membered rings. The predominant forma-

Table I. Radical polymerization of DVOB^a

Exptl no.	[M], vol%	Temp, °C	Time, hr	Yield, %	Anal.	
					C, %	H, %
1	10	60	24	94	68.61	6.58
2	5	60	15	96	68.70	6.61
3	5	60	7	89	68.53	6.58
4	5	60	7	81	68.74	6.57
5 ^b	5	0	72	96	68.74	6.67
6 ^b	5	0	72	96	68.91	6.65
7 ^c	Bulk	—	—	100	68.89	6.54
Calcd for $(\text{C}_{10}\text{H}_{11}\text{BO}_2)_n$					69.02	6.37

^a [AIBN], 1×10^{-2} mol/l; solvent, benzene.

^b Irradiated by UV lamp.

^c Spontaneous polymerization.

Figure 1. Infrared spectra: (a), Polyphenyldivinylloxyborane; (b), Phenyldivinylloxyborane.

Table II. Properties of PVA derived from poly(DVOB)

Sample no. ^a	Yield of PVA, % ^b	1,2-Glycol content, %	DP	D ₉₁₆ /D ₈₄₉ ^c	Tacticity ^d		
					I	H	S
2	190	0.0	310	0.13	34	47	19
3	110	0.5	90	0.03	39	48	13
4	120	0.5	80	0.06	38	47	15
5	160	0.5	150	0.09	41	47	13
6	160	0.9	110	0.11	44	45	11
7	160	0.3	990	0.14	40	45	15
PVA ^e	—	1.8	500	0.27	30	47	23

^a Refer to Table I.^b Calculated on the basis of the polymerization of one vinyl group per molecule.^c Optical density ratio as a measure of syndiotacticity.^d Determined from NMR spectrum of poly(vinyl acetate).^e Commercially available. **Figure 2.** Bovey's plots for the radical polymerization of phenyldivinylxyborane.

tion of six-membered rings seems to be attributed on the one hand to the hindered rotation about the B—O bond owing to $p\pi-p\pi$ double bond character¹² and on the other hand to the ring strain in the formation of five-membered rings.

For such a case of cyclopolymerization, triad tacticities have been discussed by Bovey in terms of the following equations.¹³

Table III. Cationic polymerization of DVOB^a

Initiator	Solvent	Temp °C	Yield, %
EtAlCl ₂	Toluene	−50	99
EtAlCl ₂	Toluene	−78	89
EtAlCl ₂	Toluene	−95	88
EtAlCl ₂	CH ₂ Cl ₂	−78	90
SnCl ₄	CH ₂ Cl ₂	−78	79
SnCl ₄	Toluene	−78	34

^a [M], 10 vol%; [initiator], 0.1 mol/l; 3 hr.

$$I = \sigma_1 \sigma_2$$

$$H = \sigma_1 + \sigma_2 - 2\sigma_1 \sigma_2$$

$$S = (1 - \sigma_1)(1 - \sigma_2)$$

The symbols σ_1 and σ_2 represent the probabilities of the isotactic monomer placement in alternating intramolecular and intermolecular propagating step, respectively. Calculations from the results of Table II give $\sigma_1 = \sigma_2 = 0.6-0.7$. Since the value of σ_1 happened to be nearly equal to σ_2 , the above equations incidentally reduced to the Bovey's single parameter equations.¹⁴ Bovey's plots are shown in Figure 2. Data indicate that the isotactic propagation is somewhat favored. Such a tendency has been reported in the radical polymerization of methacrylic anhydride, although the cyclization did not take place completely.^{13,15} We do not have a satisfactory explanation for the fact that both σ_1 and σ_2 were larger than 0.5.

DVOB could also be polymerized by typical cationic initiators. The results are shown in Table III. The IR spectra of these polymers were similar to those of radical polymers showing no residual vinyl groups. The cationic polymers, however, were insoluble in common solvents and could not be converted into PVA even by repeated and prolonged hydrolysis, showing that these polymers were highly cross-linked. Thus, no information on the stereo-regulation of the cationic polymerization could be obtained.

Polymerization of Chlorophenylvinylxyborane (VOBCl)

Results of the polymerization of VOBCl are shown in Table IV. VOBCl was polymerized by radical initiators. The IR spectra of the monomer and the products are shown in Figure 3 and the results of the elemental analysis of

Table IV. Polymerization of VOBCl

Exptl no.	Initiator ^a	Solvent	[M], vol%	Temp, °C	Time, hr	Yield, %
1 ^b	AIBN	Benzene	10	60	24	10
2	BPO	—	Bulk	60	42	67
3	DBPO	—	Bulk	60	42	58
4 ^c	DBPO	—	Bulk	60	42	75
5 ^d	EtAlCl ₂	Toluene	20	-78	3.5	(46) ^e
6 ^d	EtAlCl ₂	CH ₂ Cl ₂	20	-78	24	(67) ^e
7 ^d	EtAlCl ₂	Hexane	20	-78	24	(69) ^e
8 ^d	EtAlCl ₂	Toluene	20	-78	24	(59) ^e
9	SnCl ₄	CH ₂ Cl ₂	20	-78	3.5	0 ^f
10	SnCl ₄	CH ₂ Cl ₂	20	-78	24	0 ^f
11	BF ₃ OEt ₂	CH ₂ Cl ₂	20	-78	24	0 ^f
12	BF ₃ OEt ₂	Toluene	20	-78	24	0 ^f

^a Radical initiator, 0.5 mol% per monomer; cationic initiator, 0.2 mol/l; AIBN, α, α' -azobisisobutyronitrile; BPO, benzoyl peroxide; DBPO, di-*t*-butyl peroxide.

^b Colored orange.

^c [DBPO], 5 mol% per monomer.

^d Colored reddish-brown and precipitates formed.

^e Products were not polymers.

^f Monomer was recovered.

Figure 3. Infrared spectra: (a), polymer of chlorophenylvinylxyborane initiated with BPO; (b), reaction product of chlorophenylvinylxyborane initiated with EtAlCl₂; (c), chlorophenylvinylxyborane.

the radical polymers are tabulated in Table V.

The IR spectrum of the radical polymer was quite similar to that of poly(DVOB), which is shown in Figure 1. In the NMR spectrum, the integral intensity ratios of $\text{CH}_2:\text{CH}:\text{Ph}$ were not the expected ratios of 2:1:5 but about 4:2:5. Elemental analyses of the polymers (Table V) show that the chlorine content is very much smaller than the calculated value. Consequently, the radical polymerization of VOBCl seems to occur in the following manner:

The formation of dichlorophenylborane was confirmed by the NMR measurement of the volatile parts of the polymerization mixture.

As the mechanism of the VOBCl polymerization to the cyclic structure, the possibility of disproportionation prior to the polymerization was considered. DVOB is distinguishable from VOBCl by NMR spectra since the vinyl protons show different chemical shifts. VOBCl was unchanged after 48 hr at room temperature and after 10 hr at 60°C. Therefore, VOBCl is not subjected to the disproportionation to an appreciable extent under the polymerization conditions. The cyclic structures seem to have been formed by the elimination of dichlorophenylborane from two adjacent units of the polymer during polymerization.

VOBCl was not polymerized by typical cationic initiators and the monomer was recovered. Ethylaluminum dichloride decomposed VOBCl to yield phenylboroxine.

Vinyl chloride was not detected by the study of the IR spectra of the reaction mixture, but the reaction gave a reddish-brown resinous material, which was considered to have originated

Table V. Elemental analyses of radical polymers of VOBCl

Sample no. ^a	C, %	H, %	Cl, %
1	62.35	6.43	2.54
2	66.98	6.02	1.95
3	66.13	6.12	2.62
4	65.54	6.19	1.86
Calcd for $(\text{C}_8\text{H}_8\text{BClO})_n$	57.73	4.85	21.31
Calcd for $(\text{C}_{10}\text{H}_{11}\text{BO}_2)_n$	69.02	6.37	0.00

^a Refer to Table IV.

from vinyl chloride. Such a decomposition of alkoxychloroborane in the presence of a Lewis acid has been reported.¹⁶

Spontaneous Polymerization of Diphenylvinylxyborane (VOB) and Di-*n*-butylvinylxyborane

VOB could not be isolated from the reaction mixture of chlorodiphenylborane and mercuri-diacetaldehyde, although its existence was recognized by IR spectra. Quick inspection of the supernatant liquid of the reaction mixture revealed the band of $\nu_{\text{C}=\text{O}}$ at 1640 cm^{-1} . This band faded out in about 30 min and there occurred white precipitates, which could be converted into PVA by hydrolysis. When *t*-butylcatechol or benzoquinone was used as an inhibitor of the polymerization the system became somewhat stable, but still the isolation of VOB was not successful. Di-*n*-butylvinylxyborane showed a similar behavior.

The polymer of VOB was soluble in common solvents and the IR spectra of the polymer were closely similar to that of poly(DVOB). Intensity ratios in NMR spectra were found to be $\text{CH}_2:\text{CH}:\text{Ph}=2:1:3$, instead of the expected ratios of 2:1:10 for poly(VOB). The calculated ratios for poly(DVOB) are 2:1:2.5. The results of elemental analysis also indicated the structure to be similar to poly(DVOB). The structure of the poly(VOB) may be concluded to be that shown below.

Table VI. The initiating ability of boron compounds^a

Monomer	Initiator			
	Ph ₂ BCl	Ph ₂ BCl + O ₂	Ph ₂ BO Isobu	Ph ₂ BO Isobu + O ₂
VAc	Trace	1	0	0
St	1	1	Trace	0
IsobuVE	71	57	0	0
AN	0	0	0	0

^a Monomer, 5.0 ml; initiator, 1 ml (as a 1-mol/l hexane solution); room temperature; 48 hr.

It is not probable that VOB changed to DVOB prior to the polymerization and the formed DVOB was then polymerized, since DVOB was not polymerized under the same reaction condition.

The nature of the spontaneous polymerization of VOB was investigated. Chlorodiphenylborane may act as a cationic initiator, as shown in Table VI, in which the initiating ability of the probable boron species was examined.

The effects of inhibitors on the spontaneous polymerization of VOB was studied. Triethylamine showed no inhibition effect, but among the typical radical inhibitors diphenylpicrylhydrazyl (DPPH) and benzoquinone showed considerable effect, and *t*-butylcatechol and trinitrobenzene weak effect. DPPH was quickly decolored. Consequently, the polymerization of VOB seems to take place by a radical mechanism. Radicals may be formed by a thermal initiation, because it does not seem probable from Table VI that the boron compounds—oxygen system in the reaction mixture forms radical sources.

Polymerizability of Vinyloxyboron Compounds

Taking into account that VOBCl is polymerized radically but not cationically, monovinyloxyborane compounds behave like a vinyl ester rather than a vinyl ether, contrary to the fact

that monovinyloxy compounds of the group IVb metals behave as vinyl ethers. The electron density of the vinyl group in the vinyloxy compounds is considered to be increased by the resonance effect of the oxygen atom. In the case of vinyloxyborane, the resonance between the oxygen and the vinyl group seems to be suppressed, owing to the resonance of the B—O bond. This effect may make vinyloxyboranes behave as vinyl esters.

The relatively small radical polymerizability of VOBCl may be attributed to the fact that the chlorine atom donates electrons to the boron atom to suppress the resonance of the B—O bond.¹⁷ The radical polymerizability of VOB was extraordinarily high and was higher than that of DVOB. This situation makes a marked contrast to the fact that the radical polymerizability of the group IVb elements increased with the increasing number of vinyloxy groups. This may be due to the suppression of back-donation in DVOB because of saturation of the electron-accepting capacity of the boron atom.

EXPERIMENTAL

Dichlorodiphenylborane

This compound was prepared by the reaction of tetraphenyltin and boron trichloride according to the method of Burch, *et al.*,¹⁸ and was purified twice by distillation through a Vigreux column; bp 85–87°C (38 mm) [lit.¹⁸ bp 57–58°C (10 mm)]; yield, 90%.

Chlorodiphenylborane

This compound was prepared by a series of reactions.

β -Aminoethoxydiphenylborane; mp 192–193°C [lit.¹⁹ mp 190–192°C]; yield, 88%. Isobutoxydiphenylborane was rectified through a Vigreux column; bp 129–130°C (2 mm) [lit.²⁰ 153°C (10 mm)]; yield, 81%. Chlorodiphenylborane was purified twice by distillation through a Vigreux column; bp 94–95°C (1 mm) [lit.²¹ bp 119–120°C (3 mm)].

Di-n-butylchloroborane

This compound was prepared by passing dry hydrogen chloride through tri-*n*-butylborane at 110°C;²² bp 71–72°C (23 mm) [lit.²³ bp 31°C (10 mm)].

Phenyldivinylxyborane (DVOB)

A solution of 18 g (0.11 mol) of dichlorophenylborane in 50 ml of hexane was added drop by drop into a mixture of 80 g (0.28 mol) of mercuridiacetaldehyde and 150 ml of hexane at 0°C under a nitrogen atmosphere. After the addition, the mixture was stirred at the same temperature for 4 hr and then at room temperature for 1 hr. The reaction mixture was filtered and the filtrate was twice vacuum-distilled; bp 51–52°C (2 mm); yield, 49%. The NMR spectrum of this substance showed no existence of other species, but the elemental analysis did not show satisfactory agreement with the theoretical values, probably because of the air-sensitive nature.

Anal. Calcd for $C_{10}H_{11}BO_2$: C, 69.02; H, 6.37.

Found: C, 65.24; H, 6.09.

Chlorophenylvinylxyborane (VOBCl)

This compound was synthesized by the reaction of 30 g (0.16 mol) of dichlorophenylborane and 55 g (0.16 mol) of mercuridiacetaldehyde in hexane at –10°C for 3 hr; bp 35–36°C (1.5 mm); yield, 56%.

Anal. Calcd for C_8H_8BClO : C, 57.73; H, 4.85; Cl, 21.31.

Found: C, 57.70; H, 4.76; Cl, 20.66.

Spectroscopic data of DVOB and VOBCl are summarized in Table VII.

Diphenylvinylxyborane and Di-n-butylvinylxyborane

The reaction of chlorodiphenylborane or di-*n*-butylchloroborane with mercuridiacetaldehyde

Table VII. Spectroscopic data of phenylvinylxyboranes

	PhB(OCH=CH ₂)Cl	PhB(OCH=CH ₂) ₂
IR spectrum, ^a cm ⁻¹		
$\nu_{C=C}$	1640	1645
ν_{B-O}	1350	1340
ν_{C-O}	1135	1150
δ_{CH_2}	925 (940), 873	950, 865
ν_{B-Cl}	898	—
NMR spectrum ^b		
δ_{CH_2} (ppm)	4.55, 4.93	4.33, 4.78
δ_{CH} (ppm)	7.08	6.89
J_{gem} (Hz)	1.1	1.0
J_{cis} (Hz)	5.9	5.6
J_{trans} (Hz)	13.0	13.1

^a Liquid.

^b Measured in a 10% CCl₄ solution using TMS as internal standard.

were carried out analogously to the synthesis of VOBCl. The corresponding vinylxyborane compounds could not be isolated because of the rapid polymerization of the monomer solution.

Polymerization

Radical polymerizations were carried out in ampoules. Monomer and solvent were added into an ampoule under nitrogen atmosphere, then the content was degassed and sealed under vacuum. After polymerization, the content of the ampoule was poured into dry hexane and the polymer was immediately washed with dry hexane several times by decantation of the supernatant liquid, and then dried *in vacuo* at room temperature. The polymers were purified by reprecipitation from benzene–hexane. Samples for the analysis of poly(VOBCl) were all treated under nitrogen atmosphere.

For cationic polymerizations a mixture of monomer and solvent was cooled in a Schlenk tube to the desired temperatures under nitrogen and an initiator solution was added. After the polymerization, a large amount of dry hexane was poured into the tube, and the precipitate was washed with dry hexane several times.

The attempted polymerization of VOBCl with EtAlCl₂ was led to the formation of brown crystals, which were recrystallized from toluene. The crystal showed the same IR spectrum as

that of phenylboroxine prepared by dehydration of phenylboronic acid; mp 219–220°C [lit.²⁴ mp 214–216°C].

Effect of Inhibitors on the Polymerization of Diphenylvinylxyborane (VOB)

An aliquot of the supernatant liquid of the reaction mixture containing VOB was quickly added under nitrogen atmosphere into vessels which contained various types of inhibitors in hexane. The amount of precipitated polymer was observed as a measure of the inhibition effect.

Derivation into Poly(vinyl alcohol) (PVA)

Polymers were hydrolyzed with a large excess of a 1-mol/l aqueous sodium hydroxide for 6 hr at about 60°C under occasional shaking. The homogeneous solution was dialyzed for two days; the freeze-dried PVA thus obtained did not show the existence of residual boron in the flame reaction.

Measurements

The 1,2-glycol content was determined according to the method of Harris and Pritchard.²⁵

The degree of polymerization was calculated from the specific viscosity of a 1-% aqueous PVA solution at 30°C according to the equation of Nakajima.²⁶

The triad tacticities were determined from the NMR spectra of poly(vinyl acetate) (PVAc).²⁷ PVAc was derived by acetylating PVA with a mixture of acetic anhydride and pyridine (1:2) at 90°C for 10 hr in an ampoule. The NMR spectra of PVAc were measured in 10-% chloroform solutions at 60°C using a JAPAN ELECTRON OPTICS JNM-4H-100 spectrometer.

The IR spectra were measured using a HITACHI EPI-2 spectrometer. The IR spectra of PVA were measured as films or as KBr disks.

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