

Polymerization of Benzyl Vinyl Ether with a Ziegler Catalyst and Reaction of Poly(Benzyl Vinyl Ether) with TiCl_4

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ABSTRACT: The polymerization of benzyl vinyl ether (BVE) was investigated in toluene by $\text{Et}_3\text{Al}-\text{TiCl}_4$ catalyst. When the catalyst preparation and the monomer addition were carried out at 0°C and the reaction mixture was brought to 60°C , an insoluble polymeric product was obtained together with poly(benzyl vinyl ether) (PBVE). This insoluble product was revealed to be a polymer composed of BVE and vinyl alcohol units complexed with titanium compound. This was formed by the reaction of PBVE and TiCl_4 in the catalyst system and the subsequent hydrolysis of the reaction product. Poly(vinyl alcohol) (PVA) complexed with a titanium compound was obtained by the reaction of PBVE and TiCl_4 in toluene at room temperature. When the molar ratio of TiCl_4 to PBVE was above 0.3, PBVE was completely debenzylated and became insoluble by being complexed with a titanium compound. The composition of this product was roughly estimated to be $[-\{\text{CH}_2-\text{CH}(\text{OH})-\}_6-\text{TiCl}(\text{OH})_3]_n$. The complexed PVA was soluble only in hydrochloric acid and could be converted to free PVA by reprecipitation from a solution containing acetylacetone.

KEY WORDS Benzyl Vinyl Ether / Poly(Benzyl Vinyl Ether) / $\text{Et}_3\text{Al}-\text{TiCl}_4$ / Reaction / Complexation /

Stereospecific polymerizations of vinyl ether with Ziegler-type catalysts have been reported by several authors.¹ Vandenberg² has reported that a crystalline poly(benzyl vinyl ether) (PBVE) was obtained by the polymerization of benzyl vinyl ether (BVE) using Ziegler-type catalysts. They reported that the polymer had a high melting point and was insoluble in acetone and ether. On the other hand, an isotactic poly(vinyl alcohol) (PVA) has been obtained by the debenzylation of an isotactic PBVE obtained by a $\text{BF}_3 \cdot \text{OEt}_2$ catalyst at low temperature.³

The present authors have studied the polymerization of benzyl vinyl ether (BVE) by triethylaluminum-titanium chloride and, in connection with this, the reaction of PBVE and titanium tetrachloride. No crystalline PBVE was produced by the polymerization, but the polymer obtained was one partly debenzylated and com-

plexed with a titanium compound. It was found that the debenzylation occurred by the reaction of PBVE and TiCl_4 . In this paper the results of these investigations are reported.

EXPERIMENTALS

Reagents

Benzyl vinyl ether was prepared from benzyl alcohol and acetylene by the catalysis of potassium hydroxide according to Reppe's method.⁴ The monomer obtained was treated successively with sodium, calcium hydride and lithium aluminum hydride under dry nitrogen with stirring at 60°C , and then distilled under reduced pressure: bp 59.1°C (5.4 mm); n_D^{20} 1.5162 (lit.⁴ 1.5160). The purified BVE was sealed in ampoules under dry nitrogen and stored at -20°C .

n-Butyl benzyl ether⁵ was prepared by the reac-

tion of benzyl chloride and sodium *n*-butoxide in butanol: bp 106—107°C (17 mm); n_D^{20} 1.4868.

Toluene and *n*-hexane were purified by the usual methods and stored over metallic sodium.

The triethyl aluminum used (Et_3Al) was a commercial product of the Ethyl Corporation and was used as a 30% solution in *n*-heptane without purification.

Titanium tetrachloride was also of commercial source and was used as a solution in *n*-heptane without further purification.

Boron trifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$) was purified by distillation under reduced nitrogen pressure and was used as a toluene solution.

Polymerization of BVE by a Ziegler Catalyst

An ampoule equipped with a three-way stopcock was flushed with dry nitrogen and 20 ml of toluene and 1.32 mmol of Et_3Al were introduced with hypodermic syringes. To the solution 1.32 mmol of TiCl_4 was slowly added dropwise along the wall of the vessel under dry nitrogen. After ten minutes 3 g of BVE was added and the polymerization was carried out at a desired temperature. Then the reaction mixture was cooled to room temperature and poured into 500 ml of methanol containing 0.3 ml of concentrated hydrochloric acid. After standing overnight, the polymer precipitated was collected, washed with methanol and dried *in vacuo* at room temperature. The polymer obtained was fractionated by extraction with boiling acetone into soluble (Polymer A) and insoluble (Polymer B) parts.

Polymerization of BVE by $\text{BF}_3 \cdot \text{OEt}_2$

The ampoule as mentioned above was flushed with dry nitrogen and 75 ml of toluene, 25 ml of *n*-hexane and 9.7 g of BVE were introduced. The mixture was cooled to -78°C by a Dry Ice—acetone bath and then 1 ml of precooled 5% solution of $\text{BF}_3 \cdot \text{OEt}_2$ in toluene was added. After 2.5 hours the polymerization was terminated by the addition of 5 ml of ammoniac methanol and then the mixture was poured into 300 ml of methanol. After standing overnight, the precipitated polymer was collected, washed with methanol and dried *in vacuo* at room temperature: yield 8.9 g, $[\eta]$ 3.00 dl/g (in toluene at 30.0°C).

Reaction of PBVE and TiCl_4

The polymer was dissolved in toluene at a given concentration (3.8×10^{-2} mol/l based on the monomer unit). Titanium tetrachloride was also dissolved in toluene at the same concentration as that of the polymer solution. The two solutions were mixed in various proportions at 60°C , the total volume being 40 ml, and the reaction was carried out for 4 hr at that temperature. Then the precipitate formed (Polymer D) was quickly separated by filtration, washed successively with 5 ml of toluene and 20 ml of methanol containing about 5% of water and dried *in vacuo*. The filtrate was poured into 500 ml of methanol to precipitate the polymer remaining in the solution. After standing overnight the precipitated polymer (Polymer C) was collected, washed with methanol and dried *in vacuo* at room temperature.

RESULTS

Polymerization of BVE by a Ziegler Catalyst

The polymerization of BVE by the Et_3Al — TiCl_4 catalyst was carried out by varying the temperature at the catalyst preparation and at the monomer addition. The results are shown in Table I. The rate of polymerization was extremely low at -78°C . Such a very low activity of the Ziegler catalyst at low temperature is generally observed in the polymerization of olefin by this catalyst. At above 0°C the polymerization proceeded smoothly and gave the polymer in good yield. Usually the polymers (Polymer A) obtained were soluble in acetone as well as in benzene and toluene but insoluble in methanol, ethanol and water. These were glassy solids in yellow color and liquefied when warmed below 50°C . Their infrared spectra were identical to that of PBVE obtained by the $\text{BF}_3 \cdot \text{OEt}_2$ catalyst. The intrinsic viscosities of the polymer solutions were in a range of 0.1—0.2.

On the other hand, the formation of an insoluble polymer was observed when the monomer was added to the catalyst prepared at room temperature and then the mixture was heated to 60°C . In appearance the reaction mixture was homogeneous during the polymerization as if the polymer formed was wholly dissolved in the reaction medium. However, after the precipitation of

Polymerization of Benzyl Vinyl Ether with Ziegler Catalyst

 Table I. Polymerization of BVE by a Ziegler catalyst^a

Catalyst	Temp. at monomer addition (°C)	Polymerization		Polymer yield (%)	
		Temp. (°C)	Time (hr)	Total	Polymer B
Et ₃ Al—TiCl ₄ ^b	-78	-78	28	21	0.5
	0	0	4	83	Trace
	0	60	4	72	42.6 ^e
Et ₃ Al—TiCl ₄ ^c	25	60	4	84	Trace
	0	60	4	78	0.7
Et ₃ Al—β-TiCl ₃ ^d	-78	-78	6	3	Trace
	0	60	4	59	Trace

^a Monomer, 2.9 g; Solvent (toluene), 20 ml; Et₃Al, 1.32 mmol; Ti compound, 1.32 mmol.

^b Prepared at room temperature.

^c Prepared at 110°C.

^d β-TiCl₃ was prepared by the reaction of Et₃Al and TiCl₄ (1:1) at 98°C.

^e Elementary analysis of this part [Found: C, 75.2; H, 7.3; ash 3.5. Calcd for PBVE (C₉H₁₀O): C, 80.6; H, 7.5.].

the polymer in methanol a part of it became insoluble not only in toluene but also in most of the usual organic solvents. This insoluble fraction (Polymer B) was separated from the soluble one (Polymer A) by fractionation with boiling acetone. Polymer B was elastic and gradually decomposed above 150°C. Its infrared spectrum was practically identical with that of Polymer A except an absorption at 3500 cm⁻¹. This was completely dissolved in boiling cyclohexanone after being refluxed for several hours. From the solution a soluble polymer was recovered

by pouring it into a large amount of methanol. This polymer had almost the same properties as those shown by polymer A, that is, color, softening point, solubility, solution viscosity, and IR spectrum except the band at 3500 cm⁻¹.

The polymerization of BVE was also carried out using TiCl₄, Et₃Al, TiCl₃, and Et₂AlCl as catalysts which are supposed to be the components of the Ziegler catalyst. The results are shown in Table II. No polymer was obtained from the Et₃Al catalyst, but an acetone-soluble polymer was formed by the others. The poly-

 Table II. Polymerization of BVE with various catalysts^a

Catalyst	Polymerization		Polymer yield (%)	
	Temp. (°C)	Time (hr)	Total	Acetone-insoluble part
TiCl ₄	-78	6	42.8	0.0
"	-78	6	27.4	0.2
"	12	6	76.7	1.9
"	60	4	59.5	15.8
β-TiCl ₃	-78	4	4.5	Trace
"	60	4	19.2	1.1
Et ₂ AlCl	-78	4	2.9	0.0
"	60	4	76.2	0.0
Et ₃ Al	-78	4	0.0	0.0
"	60	4	0.0	0.0

^a Monomer, 2.9 g; Solvent (toluene), 20 ml; Catalyst, 1.32 mmol.

merization by $TiCl_4$ also gave a small amount of acetone-insoluble polymer, especially at elevated temperatures.

Reaction of PBVE and $TiCl_4$

The reaction of PBVE and $TiCl_4$ was investigated in order to elucidate the formation of insoluble polymer in the polymerization of BVE with the $TiCl_4$ - $AlEt_3$ catalyst. As Polymer A was usually contaminated with inorganic sub-

stances originating in the catalyst, the polymer obtained by $BF_3 \cdot OEt_2$ was mainly used in the reaction.

The results of the reactions of $TiCl_4$ and PBVE obtained by $BF_3 \cdot OEt_2$ are shown in Figure 1. Similar results were obtained in the reactions of $TiCl_4$ and the acetone-soluble polymer (Polymer A) obtained by a Ziegler catalyst.

When the molar ratio of $TiCl_4$ to PBVE (based

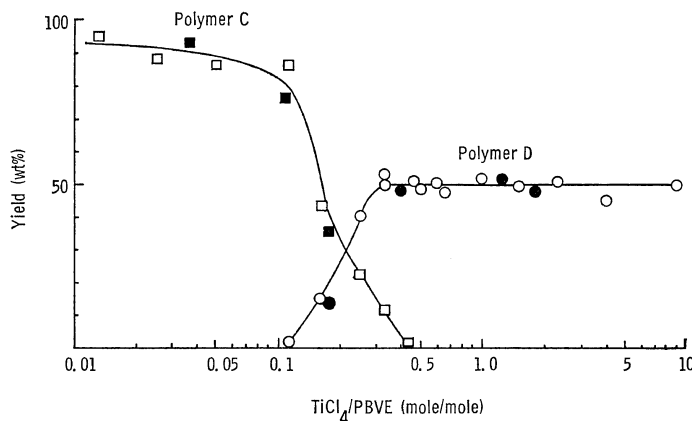


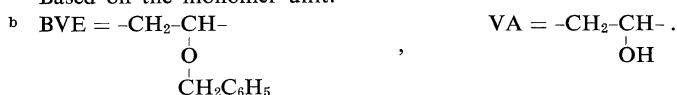
Figure 1. The reaction of PBVE and $TiCl_4$. Yield of the reaction product vs. $TiCl_4/PBVE$ ratio.

The solid symbols designate the data for the reaction products of Polymer A.

Table III. Elementary analysis and supposed compositions of the reaction products of PBVE and $TiCl_4$

Classification	$TiCl_4/PBVE$ (mol/mol)	Elementary analysis (%)				$(BVE)_m(VA)_nTiCl_k(OH)_{4-k}^b$		
		C	H	Cl	Ti	m	n	k
Polymer D	9.0	38.2	7.0	4.6	12.4	0.2	5.5	0.5
	4.0	36.0	6.9	6.3	13.3	0.1	5.0	0.6
	2.3	34.0	7.0	8.7	11.1	0	5.9	1.1
	1.5	31.9	6.9	10.0	11.3	0	5.5	1.2
	0.6	33.5	6.9	7.8	13.0	0	5.1	1.2
	0.46	36.3	6.8	7.9	11.2	0	6.4	1.0
	0.25	60.6	6.8	3.2	7.1	3.2	2.8	0.6
Polymer C	0.25	63.1	7.3	3.1	4.3	4.8	7.6	1.0
	0.11	75.7	7.5	0.9	1.5	21.3	4.5	0.8
	0.05	77.8	7.4	0.0	1.3	26.4	0.9	0
	0.013	79.3	7.5	0.0	0.7	50.1	0	0

^a Based on the monomer unit.



Calcd for $(VA)_6TiCl(OH)_3$: C, 33.9; H, 6.5; Cl, 10.0; Ti, 13.5.

Calcd for BVE: C, 80.6; H, 7.5.

on the monomer unit) was small, the product (Polymer C) was soluble in the reaction mixture, but an insoluble product (Polymer D) was formed by increasing the ratio above 0.1. When the ratio was 0.3 and above, PBVE was exclusively converted to Polymer D. The elementary analyses of the reaction products are listed in Table III.

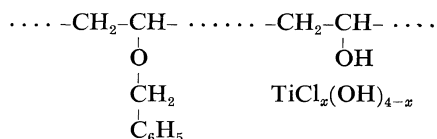
Polymer D was white powder and decomposed gradually above 210°C. It was insoluble in the usual organic solvents including benzene, toluene, cyclohexanone, and dimethyl sulfoxide. It was swollen in water and soluble in 1*N* hydrochloric acid. Most of the insoluble products (Polymer D) showed no absorption band due to the benzyl group in their IR spectra and contained considerable amounts of chlorine and titanium as shown in Table III. When Polymer D was reprecipitated five times by pouring the solution in 1*N* hydrochloric acid into methanol, the amounts of titanium decreased to about one-fifth of the original. When reprecipitation was performed from the solution containing acetylacetone, titanium and chlorine in the polymer decreased to trace amounts, and the polymer became soluble in water. This water soluble product was proved to be PVA by elementary analysis and the infrared spectrum.

Polymer C which had been in solution in the reaction of TiCl₄ and PBVE, became insoluble when it was once precipitated in methanol. The precipitated product was insoluble in usual organic solvents such as benzene, toluene, and acetone, as well as in water and hydrochloric acid, and showed an infrared absorption due to the benzyl group. Polymer C also contained titanium and chlorine as shown in Table III. However, these were not removed by the treat-

ment with acetylacetone in 1*N* hydrochloric acid, probably because of the insolubility of the polymer.

The mixture of *n*-butyl benzyl ether and TiCl₄ (5:1 mol/mol) was heated at 60°C for 2 hours. The product was distilled under reduced pressure, and the residual material was reprecipitated from the benzene solution by methanol and dried *in vacuo*. The results are summarized in Table IV, which shows that the ether was cleaved to benzyl chloride and TiCl(OBu)₃ and a part of the former was polymerized to polybenzyl.

The observations described above suggested that the reaction product of TiCl₄ and PBVE was a polymer formed by the partial or complete debenzilation of PBVE and complexed with a titanium compound. It may be composed of vinyl alcohol units and hydroxy titanium chloride with or without BVE units as follows



The compositions of the products were roughly estimated from the elementary analyses and are listed in Table III. When a small amount of TiCl₄ was used, most of the product remained in solution with only a slight degree of debenzilation. The extent of debenzilation was increased by increasing the amount of TiCl₄ used. As debenzilation reduces the molecular weight of the product, the amount of completely debenzylated product reached only a half of the amount of the starting PBVE as shown in Figure 1.

Table IV. Reaction products of *n*-butyl benzyl ether and TiCl₄^a

Product	Bp (°C/mm)	Yield (g)	Elementary analysis (%)			Remarks
			C	H	Ti	
I	65—66(13)	3.8	—	—	—	Benzyl chloride ^b
II	130—135(3)	4.8	48.5	8.9	15.0	TiCl(OBu) ₃ ^c
III	Residue	2.2	93.1	6.9	—	(C ₇ H ₆) _n ^d

^a *n*-Butyl benzyl ether, 0.1 mol; TiCl₄, 0.02 mol; Temperature, 60°C; Time, 2 hr.

^b Identified from the infrared spectrum.

^c Calcd for C₁₂H₂₇O₃TiCl: C, 47.6; H, 9.0; Ti, 15.8.

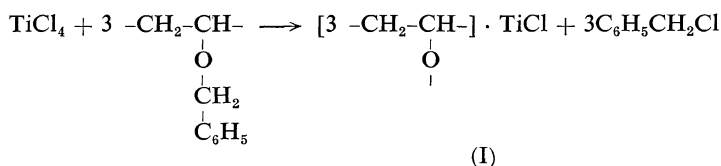
^d Calcd for (C₇H₆)_n: C, 93.3; H, 6.7. Identified also by infrared spectroscopy using an authentic sample prepared by the reaction of benzyl chloride and Et₂AlCl.

DISCUSSION

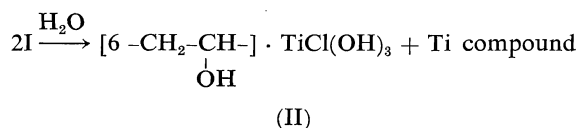
It was observed that the formation of insoluble polymer (Polymer B) from BVE by $\text{Et}_3\text{Al}-\text{TiCl}_4$ is attained only in the case where the catalyst preparation and the monomer addition are done at low temperature and then the reaction mixture is brought to high temperature.

It is well known that the reaction products of equimolar amounts of TiCl_4 and Et_3Al are TiCl_3 and Et_2AlCl at high temperature. However, when the reaction is carried out at low temperature, partially unreacted Et_3Al and TiCl_4 may possibly remain in the reaction mixture.⁷ Such a catalyst system may rapidly cause the polymerization of BVE by cationic species such as Et_2AlCl , TiCl_4 and/or TiCl_3 to give a soluble polymer of this monomer. Among them TiCl_4 gave an insoluble polymer above 0°C (Table II).

From these facts it seems to be clear that when insoluble polymer is formed by the action of a Ziegler catalyst, a part of the TiCl_4 used remains unreacted and the PBVE formed is attacked by this TiCl_4 at an elevated temperature.



The elementary analyses (Table III) show that the products seem to be II, which is the hydro-



titanium may be coordinated with vinyl alcohol units in different polymer chains resulting in the cross-linking of the polymers. In the above reaction polybenzyl might be derived from benzyl chloride by TiCl_4 , but it was not obtained. Probably the low concentrations of these chlorides in the reaction mixture gave this polymer only in a quite small amount or with so low a molecular weight that the polymer could not be precipitated by methanol.

The following conclusions may be derived from the above considerations. The soluble polymer

The reaction of TiCl_4 and *n*-butyl benzyl ether demonstrated that the $\text{O}-\text{CH}_2\text{C}_6\text{H}_5$ linkage of benzyl ether is easily cleaved by the $\text{Ti}-\text{Cl}$ compound to give benzyl chloride and titanium alkoxide. Stadnikoff⁸ has reported that diphenylmethane and dibenzylbenzene were obtained by the reaction of TiCl_4 and ethyl benzyl ether in benzene. Nishizaki⁹ has obtained polybenzyl by the reaction of alkyl benzyl ether with AlCl_3 or ZnCl_2 .

When TiCl_4 attacks the $\text{O}-\text{CH}_2\text{C}_6\text{H}_5$ linkage in PBVE, it forms benzyl chlorides and $\text{O}-\text{Ti}$ bonds in the polymer. The completely debenzylated product of PBVE was formed at the molar ratio of TiCl_4 to the polymer being above $1/3$, and approximately one chlorine atom remained per one titanium atom in the product (Table III). The reactivity of titanium chloride may be reduced by the substitution of the Cl atom with the alkoxy group, so that $(\text{RO})_3\text{TiCl}$ has little reactivity with the benzyl ether at the conditions employed in this work.

Consequently, the reaction of PBVE with TiCl_4 may proceed as follows

lyzate of I by water contained in methanol used as the precipitant. In the product II

(Polymer A) obtained by the $\text{TiCl}_4-\text{AlEt}_3$ catalyst is a low molecular weight PBVE which is similar to that obtained by the usual cationic polymerization at high temperature. The insoluble and elastic polymer (Polymer B) given by the same catalyst is a slightly debenzylated one cross-linked by a titanium compound. This is produced by a small concentration of TiCl_4 and most of the benzyl groups remained in the chain. Such a polymer can be swollen in hot cyclohexanone and the titanium compound may be removed by chelation with the ketone giving a soluble poly-

mer very similar to Polymer A. Polymer C, the product in the reactions of PBVE and $TiCl_4$ at small concentrations of the latter, must be similar to Polymer B. Both Polymer B and Polymer C were soluble in the reaction mixtures. The extent of debenzilation, that is, the substitution of the benzyl group by the titanium compound, was so slight that the titanium alcoholate was not formed intermolecularly and the polymers were still soluble in the dilute solution. When the polymer is precipitated by methanol containing water, the alcoholate is hydrolyzed and the titanium will be coordinated with vinyl alcohol units in different polymer chains resulting in the cross-linking of the polymer. The increase in the concentration of $TiCl_4$ by the reaction with PBVE decreases the amount of the benzyl group in the product and increases the extent of cross-linkage by titanium compounds as a result of the formation of intermolecular alcoholate of titanium. However, if the product retains a considerable amount of the benzyl group, it is not soluble in hydrochloric acid and cannot be attacked by acetylacetone in this acid. If the product has a lot of cross-linkage and only a trace of the benzyl group, it becomes very similar to cross-linked PVA and is insoluble in cyclohexanone even at high temperature.

The PVA cross-linked with hydroxy titanium chloride, the reaction product (Polymer D) of $TiCl_4$ and PBVE, was cast as a film from its solution in hydrochloric acid. The film was rather rigid compared with that of the usual PVA, but showed only amorphous X-ray patterns. Beacham¹⁰ reported that titanium tetraalkoxide is used as a cross-linking agent for PVA. We

found that the cross-linked PVA can also be converted to PVA almost free from cross-linkage by reprecipitation from the solution in hydrochloric acid containing acetylacetone.

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