Dual Site Character of $\text{AlEt}_3\text{-ZnCl}_2\text{-CCl}_4$ Catalyst in the Copolymerization of Ethylene with Vinyl Acetate

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ABSTRACT: Copolymerization of ethylene with vinyl acetate was carried out at room temperature by the ternary catalyst system consisting of equimolar amounts of AlEt_3 , ZnCl_2 and CCl_4 . By solvent fractionation and thin layer chromatography analysis, the copolymerization product was found to consist of two different copolymer fractions. One was the 1:1 alternating copolymer and the other was identified with the copolymer produced by the usual free radical initiator under the same reaction conditions. Two different catalyst sites were assumed, *i.e.*, the site of the usual free radical polymerization and the one responsible for the 1:1 alternating copolymerization. The addition of pyridine to the ternary catalyst system decreased mainly the yield of the 1:1 alternating copolymer fraction. Therefore, it was suggested that the coordination of monomer was essential for the catalyst site of the alternating copolymerization.

KEY WORDS Ethylene / Vinyl Acetate / Triethylaluminum / Zinc Chloride / Carbon Tetrachloride / Thin Layer Chromatography / Radical Scavenger / Alternating Copolymer / Co-ordination Polymerization / Lewis Base /

Recent findings of the 1:1 alternating copolymers of vinyl monomers with olefin¹ and diene² have aroused the interest of many workers. In these cases, however, the vinyl monomers were confined to the so-called conjugative type, such as acrylonitrile and methyl methacrylate. We have already reported the formation of a 1:1 alternating copolymer of ethylene with vinyl acetate (VAc) by the ternary catalyst system of $\text{AlEt}_3\text{-ZnCl}_2\text{-CCl}_4$.³

The present paper describes further new observations of the catalyst behavior of this ternary system in the copolymerization of ethylene with VAc. The most important finding is that the copolymerization product is a mixture of the 1:1 alternating and the random copolymers. This fact is taken to suggest that there are two different catalyst sites in the ternary system, one is responsible for the 1:1 alternating copolymerization and the other is for the usual random copolymerization of free radical mechanism.

EXPERIMENTAL

Reagents

AlEt_3

A commercial reagent was rectified under reduced nitrogen pressure, bp 66–67°C (3 mm).

ZnCl_2

A commercial reagent was dried *in vacuo* at 200°C prior to use.

CCl_4

A commercial reagent was dried and rectified on phosphorous pentaoxide, bp 76.0–76.5°C.

Tetrahydrofuran (THF)

A commercial reagent was dried and rectified on sodium dispersion, bp 65.5–66.0°C.

VAc

A commercial reagent was purified by the usual method.

Ethylene

A commercial gas sample in a cylinder was used without further purification.

Preparation of Catalyst System

In a 100 ml flask a solution of AlEt_3 (2.85 g, 25 mmol) in 25 ml of THF was mixed with a solution of ZnCl_2 (3.4 g, 25 mmol) in 25 ml of THF under nitrogen at –78°C. Then a solution of CCl_4

(3.85 g, 25 mmol) in 25 ml of THF was added dropwise, and the mixture was allowed to warm to room temperature in one hour and was used as soon as possible. The catalyst solution thus prepared was colorless and transparent. The catalyst activity of the ternary system was decreased gradually by standing even at room temperature.

Polymerization

The standard procedure of polymerization was as follows:

By using a syringe 15 ml of catalyst solution was placed in a 50 ml pressure vessel under nitrogen, to which 5 ml (54 mmol) of VAc was added. Then 7 g (250 mmol) of ethylene was compressed to the vessel in three minutes under a pressure of 60 kg/cm². In several runs, an ampoule containing VAc was broken by ethylene pressure, and the two monomers were brought into contact with the catalyst simultaneously. However, no essential difference between the ampoule method and the standard procedure was observed. The polymerization vessel was kept standing at room temperature. After polymerization the reaction mixture was treated with methanol containing a small amount of dil. aqueous HCl and the copolymerization product was extracted by methylene chloride and was isolated by the evaporation of the solvent.

Thin Layer Chromatography (TLC) of the Copolymerization Product

The TLC analysis of the copolymerization product was performed by a procedure similar to that proposed by Inagaki *et al.*⁴

Stationary Phase

One part of silica gel (GF₂₅₄ Merck AG, Darmstadt) was slurried with two parts of distilled water and applied as the stationary phase on a glass plate. The gel layer was activated at 110°C for 1 hr immediately before use. A plate (20 × 5 cm²) bearing layer 0.25 mm thick was used for qualitative analysis and a special (20 × 20 cm²) bearing layer 1 mm thick was employed for quantitative purposes.

Development Procedure

A methylene chloride solution of copolymer was spotted on the starting point (2.0 cm from the edge) by using a microsyringe so that each spot contained *ca.* 5 μg of sample. After devel-

opment in a closed bath at room temperature the solvent was removed by heating the plate at 110°C for 1 hr and then the developed spot was stained by sulfuric acid, *i.e.*, 20% of aq. sulfuric acid was sprayed onto the developed plate and then the plate was heated.

For quantitative experiment *ca.* 50 mg of the sample was mounted as a narrow band at the starting line of a special plate (20 × 20 cm² in size and 1 mm in layer thickness) by microsyringe. After development, each gel layer on which the separated sample was located was scraped off and subjected to solvent extraction with acetonitrile. The total recovering yield was over 95%.

NMR Spectra

NMR spectra of the product copolymers were taken by an instrument of 60 MC Model 60A of Japan Electron Optics Lab. Co. using tetramethylsilane as internal standard. The ratio of ethylene to VAc units in the copolymer was obtained from the peak area ratio of the peak at τ 5.10 (methine proton) or at τ 7.9 (acetyl protons) of VAc units to the multiplet from τ 8.1 to 9.0 (methylene protons) of ethylene and VAc units.

Molecular Weight

The molecular weight of the copolymer was measured by an instrument of vapor pressure osmometer type 302 of Mechrolab Co. in chloroform at 30.0°C.

RESULTS AND DISCUSSION

Copolymerization of ethylene (7 g, 250 mmol, 60 kg/cm²) with VAc (5 ml, 54 mmol) was performed at room temperature by the ternary catalyst system of AlEt₃-ZnCl₂-CCl₄ (5 mmol of each component) in 15 ml of THF for 16 hr. By extraction with methylene chloride, 3.08 g of total copolymerization product was obtained, whose average composition by NMR analysis was ethylene/VAc=2.1/1. As shown in Figure 1, the NMR spectrum of the total product has a singlet peak at τ 8.72 which is ascribed to the long methylene protons, $-(\text{CH}_2)_n-$, $n \geq 4$. This fact means the presence of sequences consisting of more than two ethylene units in the gross copolymerization product.

The gross product was then fractionated by

Figure 1. NMR spectrum of the gross copolymer of ethylene with VAc by ternary catalyst (CDCl_3 solution).

Table I. Solvent fractionation of the gross copolymer^a of ethylene with VAc (2.1/1)

Fraction	Copolymer	
	Recovered (wt %)	Ethylene/VAc (molar ratio)
PE soluble	34.8	3.1/1
PE- CH_3OH (5/1) soluble	17.4	2.4/1
PE- CH_3OH (5/1) insoluble	37.6	1/1

^a Copolymerization conditions: Catalyst, $\text{AlEt}_3\text{-ZnCl}_2\text{-CCl}_4$, 5 mmol each; THF, 15 ml; Ethylene, 7 g (250 mmol); VAc, 5 ml (54 mmol); Time, for 16 hr; Temp., at room temp., Yield, 3.08 g.

petroleum ether (PE) and PE/methanol mixture (Table I). The compositions of three fractions, PE-soluble, PE/methanol-soluble and PE/methanol-insoluble fractions, were analyzed by NMR. The PE-soluble and PE/methanol-soluble fractions were rich in ethylene units, whereas the PE/methanol insoluble fraction contained equimolar amounts of ethylene and VAc units. Further, the NMR spectrum of the PE/methanol-insoluble fraction did not possess the peak of long methylene protons at τ 8.72. The combination of these two findings, the equimolar composition and the absence of sequence of more than two ethylene units, leads to the structure of 1:1 alternating copolymer. These results of fractionation are taken to suggest that the gross copolymerization product consists of two types of copolymer, *i.e.*, the 1:1 alternating copolymer and the usual ethylene rich copolymer.

By means of thin layer chromatography (TLC)

Figure 2. Thin layer chromatograms of ethylene/VAc copolymer by ternary catalyst compared with those of reference homopolymers.

- ① Poly-VAc.
- ② Ethylene-VAc copolymer by $\text{AlEt}_3\text{-ZnCl}_2\text{-CCl}_4$.
- ③ Polyethylene.

analysis, the copolymerization product was separated more distinctly into the 1:1 alternating and ethylene rich copolymer fractions. By butyl acetate/ethyl acetate (4/1) mixture the copolymerization product was developed into two spots, A and B (Figure 2 a). At the same time, two homopolymers of ethylene and VAc were also developed. Spot A was close to the spot of polyethylene, and spot B as well as the spot of poly VAc were on the starting line. The R_f value of spot A, however, was definitely different from that of the ethylene homopolymer. Therefore, the spot A fraction was a real copolymer and did not contain the ethylene homopolymer. Spot B was differentiated from the spot of the VAc homopolymer by the second development with straight ethyl acetate (Figure 2 b). In the second development, spot B was developed till nearly the top of the second solvent front, whereas the spot of poly-VAc remained on the starting line.

The compositions of the fractions of spots A and B were determined by the quantitative TLC analysis. A fairly large amount of a sample of the gross polymer was mounted as a band on the starting line of a plate ($20 \times 20 \text{ cm}^2$ of size and 1 mm of silica gel thickness) and was developed by butyl acetate/ethyl acetate (4/1) mixture. Then the two portions of gel layers corresponding to the bands of the starting line (spot B) and of the line equivalent to R_f of spot A were scraped off, separately, and each of them was extracted with

Table II. Results of quantitative TLC analysis of ethylene/VAc copolymer^a

	Copolymer		
	wt (%) ^b	Ethylene/VAc (molar ratio)	MW ^c
Fraction A	48	3.0/1	824
Fraction B	52	1.0/1	612

^a Copolymerization conditions: Catalyst, AlEt₃-ZnCl₂-CCl₄, 5 mmol each; THF, 15 ml; Ethylene, 7 g (250 mmol); VAc, 5 ml (54 mmol); Time, for 16 hr; Temp., at room temp., Yield, 3.08 g.

^b Relative percentage to total recovered copolymer.

^c Molecular weight by VPO in chloroform at 30.0°C.

Figure 3. Nmr spectra of ethylene/VAc copolymer fractions separated by quantitative TLC analysis (CDCl₃ solution).

a: Fraction A, b: Fraction B.

acetonitrile. The compositions as well as the molecular weights of the two fractions are shown in Table II. Fraction A is the ethylene rich copolymer and fraction B is an equimolar copolymer. In addition, the absence of the peak at τ 8.72 in the NMR spectrum of fraction B is shown in Figure 3. These findings are taken to assign the 1:1 alternating copolymer structure to fraction B. In our previous study,³ only the PE/methanol insoluble fraction (fraction B of TLC analysis) was isolated and was erroneously regarded as the whole product of copolymerization.

As to the mechanism of the formation of fraction A, it has been interestingly found that the R_f value of fraction A was equal to that of copoly-

Figure 4. Thin layer chromatogram of ethylene/VAc copolymers.

① Ethylene/VAc copolymer by benzoyl peroxide.

② Ethylene/VAc copolymer by AlEt₃-ZnCl₂-CCl₄.

mer by the usual free radical initiator. Under the same reaction conditions except for the reaction temperature, a copolymerization was carried out by the benzoyl peroxide initiator at 70°C. The result of TLC analysis is shown in Figure 4. The usual radical copolymer gave only one spot and its R_f value was the same as that of the ethylene rich fraction of copolymerization by the ternary catalyst system. The molecular weight of the copolymer obtained by the benzoyl peroxide initiator was much higher than that of the ethylene rich fraction by the ternary catalyst system. However, it is known that the R_f value of TLC is independent of the molecular weight difference.⁴ These results suggest that the fraction A copolymer is formed by the usual free radical copolymerization.

Furthermore, the effects of radical scavengers and Lewis bases are significant from the mechanistic stand-point. Several radical scavengers, nitrobenzene (1 mmol), *p*-*t*-butylcatechol, hydroquinone, benzoquinone, chloranil, and DDPH (each 2.5 mmol) inhibited the formations of both fractions A and B in the polymerization of the standard recipe (see Experimental Section). Therefore, the course of polymerization leading to the 1:1 alternating copolymer (fraction B) may also be of a radical mechanism. However,

Figure 5. Thin layer chromatogram of ethylene/VAc copolymers.

① Ethylene/VAc copolymer by AlEt₃-ZnCl₂-CCl₄ (1:1:1).

② Ethylene/VAc copolymer by AlEt₃-ZnCl₂-CCl₄-pyridine (1:1:1:1).

Table III. Effect of Lewis bases on the copolymerization of ethylene with VAc by ternary catalyst^a

Lewis base	(mmol)	Yield (g)
Triphenylphosphine	5	0
Acetylacetone	5	0
Pyridine	5	1.12
α,α' -Dipyridyl	5	0.56

^a Copolymerization conditions: Catalyst, $\text{AlEt}_3\text{-ZnCl}_2\text{-CCl}_4$, 5 mmol each; THF, 15 ml; Ethylene, 7 g (250 mmol); VAc, 5 ml (54 mmol); Time, for 16 hr; Temp., at room temp.

Table IV. Results of quantitative TLC analysis of ethylene/VAc copolymers^a

Catalyst	Fraction A (Ethylene rich copolymer)		Fraction B (1:1 alternating copolymer)	
	(g)	(%)	(g)	(%)
$\text{AlEt}_3\text{-ZnCl}_2\text{-CCl}_4$ (1:1:1)	1.48	48	1.60	52
$\text{AlEt}_3\text{-ZnCl}_2\text{-CCl}_4\text{-Pyridine}$ (1:1:1:1)	1.02	91	0.10	9

^a Copolymerization conditions: Catalyst, 5 mmol each; THF, 15 ml; Ethylene, 7 g (250 mmol), VAc, 5 ml (54 mmol); Time, for 16 hr; Temp., at room temp., Yield, 3.08 g.

the scavengers may possibly destroy the active species of alternating copolymerization by a chemical reaction but not by the function as radical scavenger. Elucidation of this problem needs further studies. The addition of Lewis base differentiated more clearly the two sites producing fractions A and B, respectively. The results of copolymerization in the presence of some Lewis bases are shown in Table III. Triphenylphosphine and acetylacetone completely stopped the copolymerization. Pyridine and α,α' -dipyridyl decreased the yield of the copolymerization product. The TLC analysis (Figure 5 and Table IV) of the product by the pyridine modified catalyst has shown that the effect of pyridine was more influential to the formation of the alternating copolymer. The amount of the ethylene rich copolymer was affected to a lesser extent. A selective poisonous effect of Lewis base toward the site of the alternating copolymerization (fraction B) may be taken to assume that the coordination of monomers is essential

Figure 6. Thin layer chromatograms of ethylene/VAc copolymers compared with those of reference homopolymers.

1st develop (AcOBu-AcOEt 1:9).

2nd develop [AcOMe-AcOEt (5:5)- H_2O (0.5%)]

- ① Poly-VAc.
- ② Ethylene/VAc copolymer (1/3) by $\text{AlEt}_3\text{-ZnCl}_2\text{-CCl}_4$.
- ③ Ethylene/VAc copolymer (2.1/1) by $\text{AlEt}_3\text{-ZnCl}_2\text{-CCl}_4$.
- ④ Polyethylene.

in this site.

The dual site character of the ternary catalyst system was also observed in the copolymerization of a lower ethylene/VAc feed ratio. A mixture of 5 g (180 mmol) of ethylene (60 kg/cm²) and 10 ml (110 mmol) of VAc was polymerized by a standard ternary catalyst system in 15 ml of THF at room temperature for 1 hr to give 3.35 g of the polymeric product. By NMR analysis the average molar ratio of ethylene/VAc units of the total product was found to be 1.0/3.0. The product was analyzed by TLC of two developments together with three reference samples, two homopolymers of ethylene and VAc and the product of the standard copolymerization (Figure 6).

The product from a lower ethylene/VAc feed ratio gave two spots B and C. Spot B of a higher R_f value coincided with the spot of the 1:1 alternating copolymer of the standard copolymerization (a higher ethylene/VAc feed ratio). Spot C, which is located between spot B and the spot of the VAc homopolymer, probably represents the VAc rich copolymer fraction. It is reasonably concluded that the copolymerization of a lower feed ratio of ethylene/VAc produces the VAc rich fraction by the usual free radical mechanism and the 1:1 alternating copolymer fraction.

The present study has shown that the ethylene/VAc copolymerization by the ternary catalyst system of $\text{AlEt}_3\text{-ZnCl}_2\text{-CCl}_4$ produces two types of copolymers, the 1:1 alternating copolymer and the copolymer corresponding to the usual free radical copolymer. These findings imply the

presences of two different sites in the ternary catalyst system.

Further experiments are needed to elucidate the mechanisms of the two different copolymerizations.

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