

Alternating Copolymerization of Ethylene with Vinyl Acetate by $\text{AlEt}_3\text{—ZnCl}_2\text{—CCl}_4$ Catalyst

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ABSTRACT: The behavior of the ternary catalyst system consisting of AlEt_3 , ZnCl_2 , and CCl_4 , which enables the copolymerization of ethylene with vinyl acetate to produce a mixture of 1:1-alternating and random copolymers was studied. By the adoption of *in-situ* catalyst preparation, whereby all the catalyst components were brought into contact in the presence of the monomers, the copolymerization product gained both in yield and in molecular weight. This was ascribable, by thin-layer chromatography analysis, to the increase in the yield and molecular weight on the part of the 1:1-alternating copolymer. Varying the feed order of the catalyst components suggested that a bimetallic complex was formed between AlEt_3 and ZnCl_2 , and that the complex so formed made an important contribution to the alternating copolymerization. The 1:1-alternating copolymer was formed with excellent selectivity by the procedure of aging the mixture of AlEt_3 with ZnCl_2 prior to the addition of CCl_4 . IR and NMR analyses further suggested that the bimetallic complex possibly has the ethyl group in a bridge across the aluminum and zinc atoms, and that vinyl acetate coordinates to the complex *via* not only the carbonyl group but also the carbon—carbon double bond to form a chelate structure.

KEY WORDS Ethylene / Vinyl Acetate / Triethylaluminum / Zinc Chloride / Carbon Tetrachloride / Thin-Layer Chromatography / Alternating Copolymer / Chelate Complex / Coordination Polymerization /

The recent discovery by Hirooka of a new method for alternating copolymerization has opened up the study of a wide variety of alternating copolymers between monomers of electron-donating and electron-accepting types.¹ In a previous paper we reported on the formation of the 1:1-alternating copolymer of ethylene with vinyl acetate (VAc) by the $\text{AlEt}_3\text{—ZnCl}_2\text{—CCl}_4$ catalyst system.² This copolymerization is characterized by a monomer combination consisting of electron-donating types only. Solvent fractionation and thin-layer chromatography analyses showed that the 1:1-alternating copoly-

mer was accompanied by a random copolymer.³ This fact suggested the coexistence of two kinds of catalytic sites in the catalyst system, *i.e.*, one responsible for the alternating copolymerization and the other for the free-radical copolymerization.

This paper presents the results of further detailed investigation into the behavior of this ternary catalyst system. The preparative conditions of the catalyst system exerted marked influence upon the selectivity, activity, and molecular weight of the 1:1-alternating copolymer. The behavior of the complex formed of AlEt_3 with ZnCl_2 was investigated by IR and NMR spectroscopy. The important role of this complex in the alternating copolymerization has been elucidated.

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EXPERIMENTAL

Reagents

AlEt₃. A commercial reagent was rectified under reduced nitrogen pressure, bp 66.0–67.0°C (3 mm).

ZnCl₂. A commercial reagent was dried *in vacuo* at 200°C prior to use.

CCl₄. A commercial reagent was dried and rectified on phosphorous pentoxide, bp 76.0–76.5°C.

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

Vinyl Acetate (VAc). A commercial reagent was purified by the usual method.

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

Preparation of Catalyst System

Two methods were adopted in preparing the catalyst system: the *pre-mixing* method where the catalyst system was prepared as usual prior to feeding the monomers, as employed in our previous experiments,^{2,3} and the *in-situ* method where the system was prepared in the presence of the monomers. The procedures, more specifically, are as follows.

Pre-mixing Preparation. In a 100-ml flask a solution of AlEt₃ (1.43 g, 12.5 mmol) in 25 ml of THF was mixed with a solution of ZnCl₂ (3.40 g, 25 mmol) in 25 ml of THF under nitrogen at –78°C. After dropwise addition of a solution of CCl₄ (1.54 g, 10 mmol) in 25 ml of THF, the mixture was allowed to warm to room temperature in a given period of time. The 15 ml of the catalyst solution were transferred with a syringe into a 50-ml pressure vessel in which a sealed glass ampoule containing 5 ml (54 mmol) of VAc had been placed. Ethylene (7 g, 250 mmol) was compressed into the vessel, causing the ampoule to crush under a pressure of 60 kg/cm².

In-situ Preparation. In the pressure vessel a solution of AlEt₃ (0.285 g, 2.5 mmol) in 5 ml of THF was mixed with a solution of ZnCl₂ (0.681 g, 5.0 mmol) in 5 ml of THF under nitrogen at a given temperature. The mixture was kept standing for a given period of time to allow completion of the complex formation. The vessel

was closed after adding 5 ml of VAc and placing in the mixture a sealed glass ampoule containing a solution of CCl₄ (0.308 g, 2.0 mmol) in 5 ml of THF. Ethylene, compressed up to 60 kg/cm², was introduced to break the ampoule, bringing the catalyst components into contact with each other in the presence of the monomers. In several of the runs, a solution of CCl₄ was mixed with a solution of ZnCl₂ and an ampoule containing a solution of AlEt₃ was broken under ethylene pressure.

Polymerization

The pressure vessel in which the copolymerization had started was kept standing at room temperature (*ca.* 20°C) for a given period of time. After polymerization, the reaction mixture was treated with methanol containing a small amount of dilute aqueous HCl, followed by extraction of the product copolymers with methylene chloride.

Thin-Layer Chromatography (TLC) of Product Copolymers

The TLC analysis of the copolymerization product was performed by a procedure similar to that proposed by Inagaki, *et al.*,⁴ and employed in our preceding paper.³

A commercial silica gel (GF254, Merck AG, Darmstadt) was used as the stationary phase. The gel layer was activated at 110°C for 1 hr immediately before use. A solution of the copolymers in methylene chloride was spotted on the starting line of the plate by using a microsyringe, with each spot made to contain *ca.* 5 μg of the sample. After development in a closed bath at room temperature the solvent was removed by heating the plate and the developed spots were stained with dilute aqueous sulfuric acid.

For a quantitative experiment a special plate (20×20 cm², with the layer 1-mm thick) was employed. By using a microsyringe *ca.* 50 μg of the sample was mounted in a narrow band on the starting line. After development, each of the bands of the gel layer into which the sample had separated was scraped off and subjected to solvent extraction with acetonitrile. The total yield recovered was over 95%.

IR Spectra

The IR spectra of the catalyst components

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Table I. Aging effect of AlEt₃—ZnCl₂—CCl₄ catalyst system in ethylene—VAc copolymerization^a

Run No.	Catalyst				Monomer feed temp, °C	Polymerization time, hr	Copolymer										
	AlEt ₃ , mmol	ZnCl ₂ , mmol	CCl ₄ , mmol	Aging time ^b , min			Gross			Fraction A (Random copolymer)			Fraction B (1:1-alternating copolymer)				
							Yield, g	Ethylene content, mol %	MW ^d	wt % ^e	g ^f	Ethylene content, mol %	MW ^d	wt % ^e	g ^f	Ethylene content, mol %	MW ^d
1. ^g	5.0	5.0	5.0	60	20	16	3.08	68	730	48	1.48	76	820	52	1.60	50	610
2.	5.0	5.0	5.0	60	20	2	Trace	—	—	—	—	—	—	—	—	—	—
3.	2.5	5.0	2.0	30	20	2	Trace	—	—	—	—	—	—	—	—	—	—
4.	2.5	5.0	2.0	10	20	2	0.35	63	1,040	—	—	—	—	—	—	—	—
5.	2.5	5.0	2.0	0 ^c	20	2	1.03	61	2,000	30	0.31	79	910	70	0.72	51	3,780

^a Copolymerization conditions: THF, 15 ml; ethylene, 7 g (250 mmol, 60 kg/cm²); VAc, 5 ml (54 mmol); temp, 20°C (room temperature).

^b Time from catalyst feed (at -78°C) to monomer feed (at room temperature).

^c Ampoule containing a solution of AlEt₃ in THF, crushed under ethylene pressure.

^d Molecular weight by VPO in chloroform at 40°C.

^e Weight percentage to total recovered copolymer as determined by quantitative TLC analysis.

^f Weight obtained by multiplying gross yield by weight percentage.

^g Experimental results shown in ref 3.

were measured with an instrument of Hitachi, Ltd., Model 215, by using a KBr solution cell (0.1 mm in thickness) under nitrogen.

NMR Spectra

The NMR spectra of the product copolymers were measured with a spectrometer of 60 MHz, Model JNM-C-60 of Japan Electron Optics Lab. Co. Ltd., using tetramethylsilane as the internal standard. The ratio of ethylene to VAc units in the copolymer was calculated from the area ratio of the peak at τ 5.10 (methine proton) or at τ 7.96 (acetyl protons) of VAc units to the multiplet from τ 8.1 to τ 9.0 (methylene protons) of ethylene and VAc units. The NMR spectra of the catalyst components were also taken at 23°C with the same instrument under nitrogen.

Molecular Weight

The molecular weight of the product copolymer was measured by a vapor pressure osmometer (VPO) Type 302 of Mechrolab Co., in chloroform at 40.0°C.

RESULTS AND DISCUSSION

The ternary catalyst system of AlEt₃—ZnCl₂—CCl₄ enables copolymerization of ethylene with VAc under mild conditions, as shown in Table I.

Our previous paper described the results of copolymerizing ethylene (7 g, 250 mmol, 60 kg/cm²) with VAc (5 ml, 54 mmol) for 16 hr at room temperature by use of the catalyst system prepared by the *pre-mixing* method,³ *i.e.*, all the catalyst components were mixed 1 hr prior to their contact with the monomers (Run No. 1).

When the reaction time was limited to 2 hr, with all the other copolymerization conditions remaining the same, only trace amounts of solid copolymers were formed (Run No. 2). Further investigations were then carried out into the conditions for the preparation of the catalyst system. It was found that the catalyst activity was greatly improved by controlling the aging time between the mixing of the catalyst components at -78°C and the feeding of the monomers at room temperature: the shorter the aging time, the greater was the activity (Runs No.

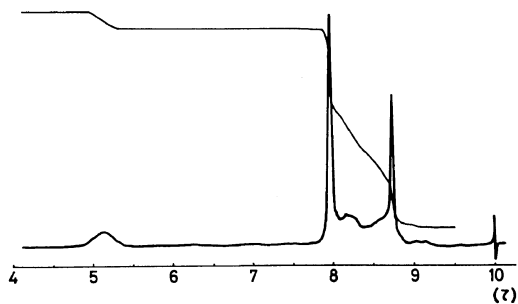


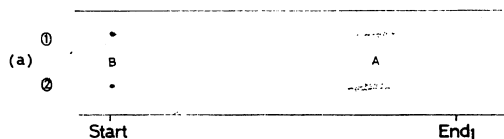
Figure 1. NMR spectrum of gross ethylene—VAc copolymer by *in-situ* prepared AlEt_3 — ZnCl_2 — CCl_4 catalyst system with AlEt_3 ampouled, CDCl_3 solution.

2—4).

The catalyst system prepared *in situ*, *i.e.*, without allowing any aging time, made possible by crushing a glass ampoule containing a solution of AlEt_3 in THF by ethylene introduced under pressure, gave the most significant activity (Run No. 5). The NMR spectrum of this total copolymerization product showed a singlet peak at τ 8.72 assignable to the long methylene linkage, as shown in Figure 1. This indicates the presence of sequences consisting of more than two ethylene units in the gross copolymers. The analysis of the NMR spectrum showed that the total product obtained by the *in-situ* catalyst system had a composition richer in VAc content than that obtained by the *pre-mixed* catalyst system. The measurement conducted with the vapor pressure osmometer also indicated an increase in molecular weight for the product by the *in-situ* catalyst system.

For detailed investigation of these interesting phenomena brought about by the adoption of the *in-situ* catalyst preparation, the gross product was subjected to thin-layer chromatography analysis. The development which was conducted with a butyl acetate/amyl acetate-(5/1) mixture on the copolymerization products obtained by the *pre-mixed* ① and *in-situ* ② catalyst systems, respectively, (Runs No. 1 and 5, Table I), gave spots at A and B, with the two spots at A showing almost identical R_f values, while the two spots at B remained on the starting line (Figure 2a). The second development conducted with straight ethyl acetate resulted in the two spots at B also having almost identical R_f values

1st develop. (AcO Bu + AcO Am , 5 : 1)



2nd develop. (AcOEt)

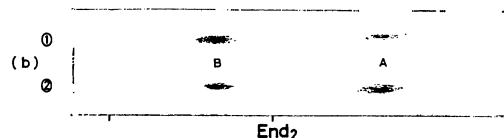


Figure 2. Thin-layer chromatograms of ethylene—VAc copolymers with ternary catalyst system, prepared by ① *pre-mixing* method, ② *in-situ* method.

(Figure 2b). The gross copolymerization product obtained by the *pre-mixed* catalyst system ① has already been shown to consist of the ethylene-rich random copolymer corresponding to spot A, and the 1:1-alternating copolymer corresponding to spot B.³ The parallel behavior of the two sets of spots strongly suggests that the copolymerization product obtained by the *in-situ* catalyst system likewise consists of random and 1:1-alternating copolymers.

The gross copolymers prepared by the *in-situ* catalyst system were then subjected to quantitative TLC analysis to determine the compositions of fractions A and B. A fairly large amount of the gross copolymer was developed by use of a special plate ($20 \times 20 \text{ cm}^2$, with a layer of silica gel 1-mm thick). The two portions of the gel layer corresponding to spots A and B were scraped off separately, and each was extracted with acetonitrile. The recovered fractions were analyzed in terms of weight percentage, composition, and molecular weight, the results are included in Table I.

The *in-situ* catalyst system clearly gave a marked increase in weight percentage, *i.e.*, selectivity for the formation of fraction B. Fraction A was identified with an ethylene-rich copolymer while fraction B was found to be an equimolar copolymer. The NMR spectra of the two fractions contrast the presence of the long methylene linkage in fraction A against its absence in fraction B, as shown in Figure 3. These findings are taken to assign the random structure

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Table II. Ethylene—VAc copolymerization^a by *in-situ* prepared catalyst system with CCl₄ in ampoule

Run No.	Aging conditions		Copolymer										
			Gross			Fraction A (Random copolymer)				Fraction B (1:1 alternating copolymer)			
	Temp, °C	Time, hr	Yield, g	Ethylene content, mol %	MW ^b	wt % ^c	g ^d	Ethylene content, mol %	MW ^b	wt % ^c	g ^d	Ethylene content, mol %	MW ^b
6	0	0	1.40	57	3,080	12	0.17	80	940	88	1.23	51	4,200
7	0	3	2.17	53	2,700	5	0.11	76	860	95	2.06	50	3,340
8	20	3	0.63	56	2,190	13	0.08	78	830	87	0.55	50	3,090
9	-20	3	1.64	59	2,660	21	0.34	77	930	79	1.30	51	4,060

^a Copolymerization conditions: AlEt₃—ZnCl₂—CCl₄, 2.5—5.0—2.0 mmol; THF, 15 ml; ethylene, 7 g (250 mmol, 60 kg/cm²); VAc, 5 ml (54 mmol); time, 2 hr; temp, 20°C (room temperature).

^b Molecular weight by VPO in chloroform at 40.0°C.

^c Weight percentage to total recovered copolymer as determined by quantitative TLC analysis.

^d Weight obtained by multiplying gross yield by weight percentage.

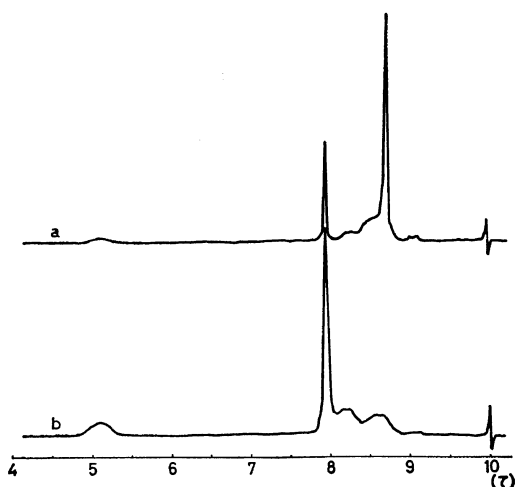


Figure 3. NMR spectra of ethylene—VAc copolymer fractions separated by quantitative TLC analysis: a, Fraction A; b, Fraction B; CDCl₃ solution; 23°C.

to fraction A, and the 1:1-alternating structure to fraction B.

It is further noteworthy that the increase in molecular weight of the gross product obtained with the *in-situ* catalyst system employed was derived predominantly from the significant increase in molecular weight on the part of the 1:1-alternating copolymer. Thus it is seen that the aging of the catalyst system affects the formation ratio between the two kinds of co-

polymers, *i.e.*, the 1:1-alternating and the random copolymers.

In order to gain more insight into the *in-situ* catalyst system, further copolymerization runs were carried out with the ampoule component AlEt₃ replaced by CCl₄, as shown in Table II. The catalyst system with CCl₄ ampouled increased the weight percentage and yield of the 1:1-alternating copolymer (Run No. 6) in greater proportions than did the system with AlEt₃ ampouled (Run No. 5, Table I). The improved selectivity and activity effected by the catalyst system of which the AlEt₃—ZnCl₂ admixed solution had to remain intact until CCl₄ was added suggest that a complex which may have formed between AlEt₃ and ZnCl₂ is involved in the alternating copolymerization.

To substantiate this inference, the admixed solution of AlEt₃ and ZnCl₂ was examined for the aging effect. When it was aged at 0°C for 3 hr, an even greater yield of the gross copolymer resulted (Run No. 7). This could be accounted for by the markedly increased activity of the alternating copolymerization, which is a clear indication of the AlEt₃—ZnCl₂ bimetallic complex assuming an important role in the formation of the alternating copolymer. On the other hand, aging of the AlEt₃—ZnCl₂ mixture at 20°C for 3 hr decreased the gross activity, which was attributable mainly to the reduced activity for the alternating copolymerization

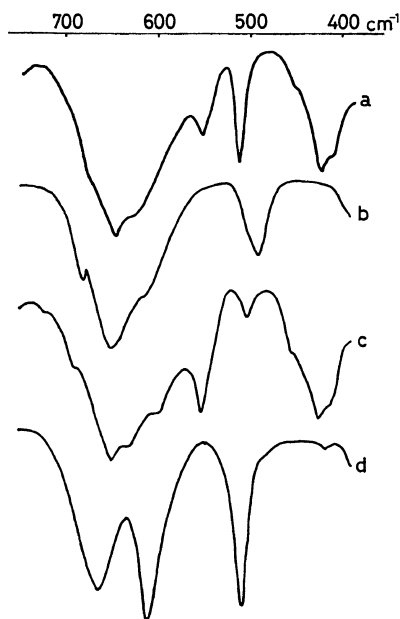


Figure 4. IR spectra comparing $\text{AlEt}_3\text{-ZnCl}_2$ complex with reference compounds: a, $\text{AlEt}_3\text{-ZnCl}_2$ (1:1, *ca.* 10 min after preparation); b, AlEt_3 ; c, AlEt_2Cl ; d, ZnEtCl ; each 0.1 molar solution of THF; 23°C.

(Run No. 8). No polymerization took place by the catalyst system where CCl_4 was added to the $\text{AlEt}_3\text{-ZnCl}_2$ mixture aged at room temperature for 24 hr; during this time the zinc metal was observed to precipitate. These facts suggest that the $\text{AlEt}_3\text{-ZnCl}_2$ bimetallic complex is of delicate stability at such temperatures. With the mixture solution aged at -20°C for 3 hr, the selectivity for the 1:1-alternating copolymer was found to decrease (Run No. 9). This possibly indicates that such low temperatures retarded the formation of $\text{AlEt}_3\text{-ZnCl}_2$ complex in THF solution.

IR and NMR spectral analyses were then carried out as further investigations into the behavior of the bimetallic complex. The IR spectrum of the 1:1 mixture of AlEt_3 with ZnCl_2 prepared under conditions similar to those employed for the copolymerization was compared with the reference spectra of AlEt_3 , AlEt_2Cl , and ZnEtCl (equimolar mixture of ZnEt_2 with ZnCl_2 in THF), as shown in Figure 4. The spectrum of the $\text{AlEt}_3\text{-ZnCl}_2$ mixture, (a), clearly

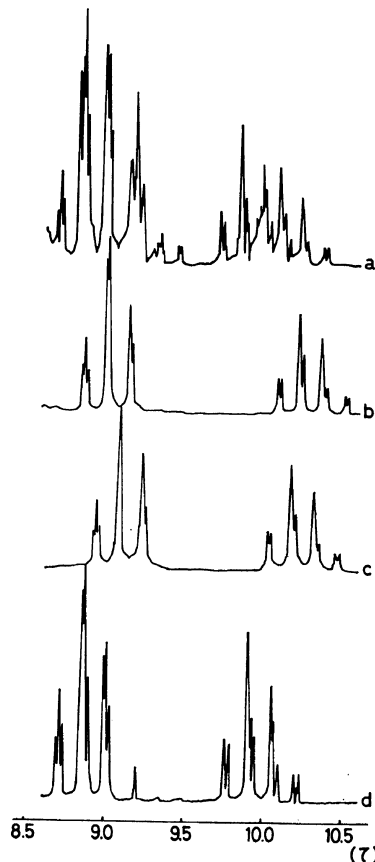


Figure 5. NMR spectra comparing $\text{AlEt}_3\text{-ZnCl}_2$ complex with reference compounds: a, $\text{AlEt}_3\text{-ZnCl}_2$ (1:1, *ca.* 10 min after preparation); b, AlEt_3 ; c, AlEt_2Cl ; d, ZnEtCl ; each 1.0 molar solution of THF; 23°C.

differs from that of AlEt_3 , (b), indicating that AlEt_3 has somehow interacted with ZnCl_2 . The possibility of the ethyl group in AlEt_3 simply interchanging with the chlorine atom in ZnCl_2 was excluded, because the spectrum of the mixture system does not fit the 1:1 overlapped spectrum of AlEt_2Cl (c) and ZnEtCl (d). These facts confirm the formation of a complex between AlEt_3 and ZnCl_2 in the mixture system.

The NMR spectrum of this complex, prepared under similar conditions, was compared with the reference, as shown in Figure 5. All the chemical shifts of the methylene protons in the ethyl groups linked to the metals were detected in fields higher than those in which the shifts of the methyl protons were detected. The

$\text{AlEt}_3\text{—ZnCl}_2$ mixture system gave the most intricate spectrum with the specific multiplet chemical shift from τ 9.0 to τ 9.5; this may be assigned to the methylene protons shifted to the lower field. The specific shift is not observable in either of the references. A report has been made on similar specific chemical shift in the spectrum obtained by the measurement of a solution of AlEt_3 in toluene at a low temperature (-80°C),⁵ where the AlEt_3 molecules associate themselves to form the dimers. The specific shift in that case has been assigned to the methylene protons of the *bridge* ethyl group in the dimer structure.⁵ Therefore, the detection of the multiplet shift in the spectrum of the $\text{AlEt}_3\text{—ZnCl}_2$ mixture system may be taken to justify visualizing the bimetallic complex with the *bridge* ethyl group fixed between the aluminum and zinc atoms.

To determine the mechanism of the alternating copolymerization by the ternary catalyst system, IR spectra of VAc in the presence of the $\text{AlEt}_3\text{—ZnCl}_2$ complex as well as in the presence of

the references were then examined. Figure 6 compares the spectrum for VAc in THF in the presence of AlEt_3 and ZnCl_2 , (a), with that for free VAc in THF alone, (b). It is noteworthy that the specific absorption peaks not only of the carbonyl group but also of the carbon—carbon double bond shifted to the lower wave number side by 20 cm^{-1} and 10 cm^{-1} , respectively, in the $\text{AlEt}_3\text{—ZnCl}_2$ mixture system. No such phenomenon was observed in any of the spectra for VAc in THF in the presence of either AlEt_3 , AlEt_2Cl , or ZnEtCl , and the two corresponding absorption peaks were quite identical with those of free VAc. This suggests that each of these references forms a firm complex with the solvent THF, and that the VAc molecules, in THF solution, undergo no interactions with either of these complexes. Thus the fact that, even in the THF solution, the two absorption peaks were observed to shift only in the presence of AlEt_3 and ZnCl_2 is suggestive of a probable bidentate coordination to the $\text{AlEt}_3\text{—ZnCl}_2$ complex not only at the carbonyl group but also at the carbon—carbon double bond in VAc.

The mixture system of VAc with the $\text{AlEt}_3\text{—ZnCl}_2$ complex was cooled and treated with methanol to decompose the complex at a low temperature (-78°C). The gas chromatography analysis performed on the treated solution showed quantitative recovery of the VAc monomer. This result provides another support to the suggestion that VAc coordinating to, but not reacting with, the $\text{AlEt}_3\text{—ZnCl}_2$ complex participates in the alternating copolymerization.

We have already elucidated that the fragments formed from CCl_4 are found incorporated in the alternating copolymer.² A separate copolymerization was attempted without the use of CCl_4 for the purpose of elucidating how it may interact with the $\text{AlEt}_3\text{—ZnCl}_2$ bimetallic complex coordinated by the VAc molecules. To the mixture solution of AlEt_3 and ZnCl_2 , aged at 0°C for 3 hr, was added VAc, then ethylene was introduced under pressure. The system, maintained at 20°C for 2 hr, yielded no copolymerization products. These facts, together with the result of the gas chromatography analysis, suggest that CCl_4 initiates the alternating copolymerization by attacking the bimetallic complex to which the VAc monomer has coordinated.



Figure 6. IR spectra comparing VAc—($\text{AlEt}_3\text{—ZnCl}_2$ complex) mixture with a reference system: a, VAc— $\text{AlEt}_3\text{—ZnCl}_2$ (1:1:1, *ca.* 10 min after preparation); b, free VAc (quite similar to the spectra obtained for the system VAc— AlEt_3 (1:1), VAc— AlEt_2Cl (1:1), or VAc— ZnEtCl (1:1)); each 0.1 molar solution of THF; 23°C .

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