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Copolymerization of Vinyl Chloride with Ethylene by the VO(OEt)$_3$-Alkylaluminum Catalyst Systems

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The copolymerization of vinyl chloride with ethylene was carried out in *n*-heptane by using the catalyst systems consisting of VO(OEt)$_3$ and AlEt$_3$, AlEt$_2$Cl, or AlEtCl$_2$ at 50°C. It was found that each of the above catalyst systems produces a random copolymer at Al/V molar ratios below 1.5; however, polyethylene is mainly obtained above the ratio of 1.5. With the VO(OEt)$_3$/AlEt$_3$ catalyst system, its good catalyst activity being in contrast with the inactivity of the Ti(O–*n*-Bu)$_4$/AlEt$_3$ catalyst system, the maximum catalyst activity was observed at the Al/V molar ratio of 0.5. The copolymerization rate decreased with an increase in the ethylene fraction in the monomer mixture, reaching a minimum value at a 80 mol% ethylene feed; however, the rate increased above this feed ratio with a further increase in the ethylene feed. The contamination of a copolymer with polyethylene which has been observed in the copolymerization by the Ti(O–*n*-Bu)$_4$/AlEt$_2$Cl or AlEtCl$_2$ catalyst system was not observed in the present case. The monomer reactivity ratios for the copolymerization by the VO(OEt)$_3$/AlEt$_3$ catalyst system were found to be r_1(vinyl chloride)$=2.48$ and r_2(ethylene)$=0.02$. The reaction between VO(OEt)$_3$ and AlEt$_3$ was investigated by means of infrared spectroscopy and gasometry, and it was found that the average valency states of the V of the catalyst system is higher than four at the Al/V molar ratio range where a random copolymer is exclusively obtained.

The copolymerization of vinyl chloride with ethylene has been drawing attention from the fundamental as well as from the industrial point of view. In previous papers[1-4] the present authors have already reported the copolymerization of vinyl chloride with ethylene by the trialkylboron/peroxide as well as by the Ti(O–*n*-Bu)$_4$/alkylaluminum catalyst systems. The copolymerization by Ziegler-Natta catalysts seems especially interesting in view of the expectation that ethylene is more susceptible to coordination polymerization than to free-radical polymerization; a copolymer richer in ethylene than that obtained from radical copolymerization could be obtained.

The present authors have found that the catalyst systems consisting of alkyl orthovanadate and alkylaluminum can copolymerize vinyl chloride with ethylene; it seems interesting to compare these results with the copolymerization results obtained by using the Ti(O–*n*-Bu)$_4$/alkylaluminum catalyst systems. In this paper, the authors wish to report the general features of the copolymerization of vinyl chloride with ethylene by the VO(OEt)$_3$/alkylaluminum catalyst systems, and also discuss briefly the reaction of the catalyst component in order to elucidate the nature of the active site-formation reaction.

Experimental

Materials. Vinyl chloride supplied by the Chisso Co. was purified by passing it through a column containing calcium chloride and then one containing phosphorous pentoxide. Ethylene supplied by the Nihon Petrochemical Co. was used without further purification. Each alkylaluminum was purified by distillation under reduced pressure and was stored as a normal solution in *n*-heptane. Ethyl orthovanadate was prepared from vanadium pentoxide and absolute ethanol according to the method of Prandtl *et al.*,[5] and was stored much like an alkylaluminum, bp 80°C/5 mmHg. The solvent was purified by shaking it with concentrated sulfuric acid and by distillation over sodium wire.

Polymerization. The reaction vessel was a 100 m*l* stainless-steel autoclave equipped with an electromagnetic agitating device. The catalyst system was

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[1] A. Misono, Y. Uchida and K. Yamada, This Bulletin, **39**, 2458 (1966).

[2] A. Misono, Y. Uchida and K. Yamada, Preprints for the International Symposium on Macromolecular Chemistry (Tokyo and Kyoto, 1966), Vol. I, p. 132.

[3] A. Misono, Y. Uchida and K. Yamada, *J. Polymer Sci.*, **B5**, 401 (1967).

[4] A. Misono, Y. Uchida and K. Yamada, This Bulletin, **40**, 2366 (1967).

[5] W. Prandtl and L. Hess, *Z. Anorg. Allgem. Chem.*, **82**, 103 (1913).

prepared by mixing $VO(OEt)_3$ and an alkylaluminum as a *n*-heptane solution in *n*-heptane at room temperature in the absence of the monomers under a pure nitrogen atmosphere; it was then aged for about one hour prior to use in the polymerization. After the autoclave had been cooled below −40°C, the inner nitrogen was evacuated. Vinyl chloride and then ethylene were introduced into the autoclave according to the method described in a previous paper.¹⁾ Then the autoclave was set in an electric heater and maintained at 50°C for three hours. The resultant products were treated and purified as has been reported in a previous paper.⁴⁾ The composition of the product was calculated from the results of elemental C and Cl analyses. The reduced specific viscosity of the polymer was measured in a 0.5 g/100 m*l* cyclohexanone solution at 30.0°C. The infrared spectrum of the polymer was measured with a Hitachi model EPI-S2 infrared spectrometer (KBr disk method). The NMR spectrum of the polymer was measured with a Nihon Denshi model C-60 high-resolution NMR spectrometer at 60 Mc and 110°C in a 10 wt/vol% monochlorobenzene solution, using tetramethylsilane as the internal standard.

Gasometric Measurements. The reaction of $VO(OEt)_3$ and $AlEt_3$ was carried out in an apparatus fitted with a side arm. A *n*-heptane solution of $AlEt_3$, stored in the side arm of the Schlenk apparatus, was added to a *n*-heptane solution of $VO(OEt)_3$ placed in the bottom of the apparatus. During the operation, the catalyst solution was kept at 20°C with stirring under a pure nitrogen atmosphere. The gaseous products were analyzed by means of gas chromatography using a column packed with silica gel at 70°C.

Results and Discussion

The Influence of the Structure of Alkylaluminum. Table 1 summarizes the results of the copolymerization of vinyl chloride with ethylene by the $VO(OEt)_3/AlEt_mCl_{3-m}$ catalyst systems at various Al/V molar ratios. Figure 1 shows the infrared spectra of the copolymerization products obtained by some of the catalyst systems shown in Table 1. As has been reported in a previous paper,⁶⁾ a random copolymer of vinyl chloride with ethylene shows a characteristic absorption at 745 cm⁻¹, an absorption which has been assigned to the methylene rocking mode of a boundary structure in the copolymer chain as follows:

$$-CHCl-CH_2-CH_2-CH_2-CHCl-$$

On the basis of the arguments presented in a previous paper,⁴⁾ it follows, from the results shown

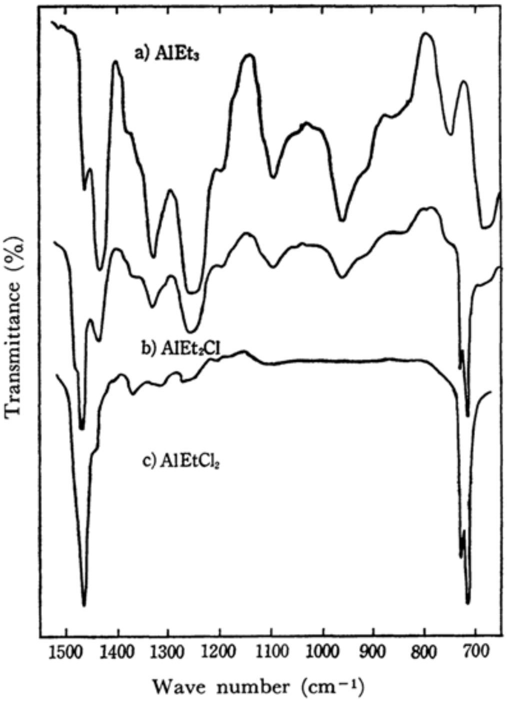

Fig. 1. Infrared spectra of copolymerization products.
a) Al/V=1.5, VCl mol%=82.3
b) Al/V=3.0, VCl mol%=14.1
c) Al/V=5.0, VCl mol%=1.0

TABLE 1. COPOLYMERIZATION RESULTS BY THE $VO(OEt)_3/AlEt_mCl_{3-m}$ CATALYST SYSTEMS

Alkylaluminum	Al/V molar ratio	Yield(%)	VCl mol% in product	Main product	η_{sp}/c (d*l*/g)
$AlEt_3$	1.5	11.3	82.3	Copolymer	0.346
$AlEt_3$	3.0	3.2	6.4	PE	—
$AlEt_3$	5.0	0.3	18.3	PE+Copolymer	—
$AlEt_2Cl$	1.5	5.8	86.6	Copolymer	0.367
$AlEt_2Cl$	3.0	13.1	14.1	PE+Copolymer	—
$AlEt_2Cl$	5.0	25.2	2.5	PE	—
$AlEtCl_2$	1.5	2.6	82.5	Copolymer	0.283
$AlEtCl_2$	3.0	18.2	2.5	PE	—
$AlEtCl_2$	5.0	15.4	1.0	PE	—

Experimental conditions: vinyl chloride, 0.3 mol; ethylene, 0.2 mol; $VO(OEt)_3$, 2.0 mmol; solvent, *n*-heptane; volume of catalyst solution, 50 m*l*; polymerization temperature, 50°C; polymerization time, 3 hr.

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6) A. Misono, Y. Uchida and K. Yamada, This Bulletin, **40**, 2696 (1967).

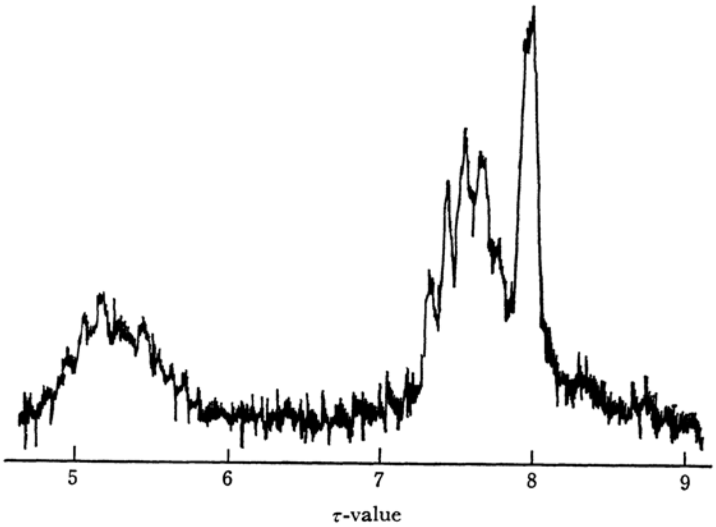

Fig. 2. NMR spectrum of a copolymer (VCl mol% = 82.3)

in Table 1 and Fig. 1, that the catalyst systems consisting of $VO(OEt)_3$ and each alkylaluminum produce random copolymers at the Al/V molar ratio of 1.5. Figure 2 shows the NMR spectrum of the copolymerization product obtained by the $VO(OEt)_3/AlEt_3$ catalyst system at the Al/V molar ratio of 1.5. The resonance peak observed at 8.35 τ has been assigned to the protons of a methylene group having a methine and a methylene group in the nearest neighbors in the copolymer chain presented above,[7] also indicating that the product consists of a random copolymer.

At the Al/V molar ratio of 3 and 5, the resultant products are composed mainly of polyethylene. However, a considerable amount of vinyl chloride was found in the products obtained by the $VO(OEt)_3/AlEt_2Cl$ catalyst system at the Al/V molar ratio of 3. The results of successive solvent extractions using tetrahydrofuran and monochlorobenzene indicate that the products consist of a random copolymer (26.0wt%) and polyethylene (74.0wt%).

The Influence of the Al/V Molar Ratio. With the $VO(OEt)_3/AlEt_2Cl$ or $AlEtCl_2$ catalyst system, the copolymer yield increases remarkably with an increase in the Al/V molar ratio at higher molar ratio, where polyethylene is the main product. These tendencies are analogous to what has been observed in the copolymerization by the $Ti(O\text{-}n\text{-}Bu)_4/AlEt_2Cl$ or $AlEtCl_2$ catalyst system. On the other hand, the copolymer yield decreases with an increase in the Al/V molar ratio when the $VO(OEt)_3/AlEt_3$ catalyst system is adopted. At Al/V molar ratio below 1.5 in the copolymerization by this catalyst system, the products consists exclusively of random copolymers with essentially the same compositions as that obtained at the ratio of 1.5.

In the copolymerization by the $VO(OEt)_3/AlEt_3$ catalyst system, the copolymer yield increases with an increase in Al/V molar ratio, reaching the maximum at the ratio of 0.5, and then it decreases continuously at ratios higher than this, as is shown in Fig. 3. It is interesting to note that $AlEt_3$, in combination with $VO(OEt)_3$, shows such a good catalyst activity in the copolymerization of vinyl chloride with ethylene in spite of the fact it is inactive in the copolymerization when combined with $Ti(O\text{-}n\text{-}Bu)_4$.

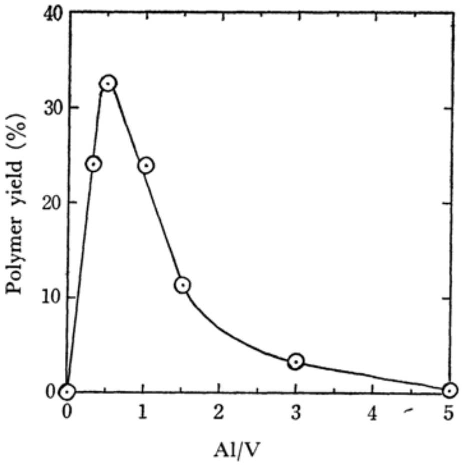

Fig. 3. Influence of the Al/V molar ratio.

Experimental conditions: vinyl chloride, 0.3 mol; ethylene, 0.2 mol; $VO(OEt)_3$, 2.0 mmol; $AlEt_3$, varied; solvent, *n*-heptane; volume of catalyst solution, 50 m*l*; polymerization temperature, 50°C; polymerization time, 3 hr.

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[7] A. Misono, Y. Uchida and K. Yamada, Preprints for the 21st Annual Meeting of Chemical Society of Japan (Osaka, 1968), No. 17313.

The Influence of the Monomer Feed Ratio. The copolymerization products obtained by using the VO(OEt)$_3$/AlEt$_3$ catalyst system at Al/V molar ratios lower than 1.5 at various monomer feed ratios consist exclusively of random copolymers, and there occurs no such contamination of the copolymer with polyethylene as has been observed in the copolymerization by the Ti(O-*n*-Bu)$_4$/alkylaluminum catalyst systems at higher ethylene feed ratios.4) Therefore, it may be considered that only one kind of active site producing random copolymers exclusively operates in the copolymerization by the VO(OEt)$_3$/AlEt$_3$ catalyst system at relatively low Al/V molar ratios. The rate of copolymerization and the reduced specific viscosity of the copolymer decrease with an increase in the ethylene feed ratio, reaching a minimum value at 80 mol% ethylene feed ratio, as is shown in Fig. 4. The facts that the copolymerization rate again increases above this ethylene feed ratio, and that ethylene homopolymerizes in the presence of the catalyst systems active in the vinyl chloride-ethylene copolymerization, are in contrast with what has been observed in the copolymerization by the Ti(O-*n*-Bu)$_4$/alkylaluminum catalyst systems.

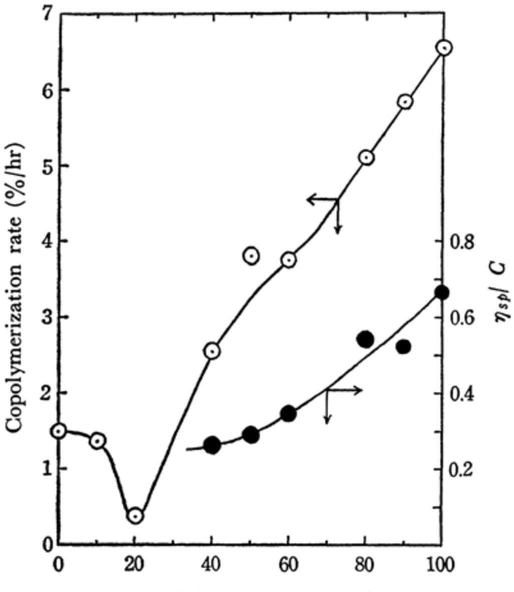

Fig. 4. Influence of monomer feed ratio. Experimental conditions: vinyl chloride + ethylene, 0.5 mol; VO(OEt)$_3$, 2.0 mmol; Al/V, 1.5; volume of catalyst solution, 50 m*l*; polymerization temperature, 50°C; polymerization time, 3 hr.

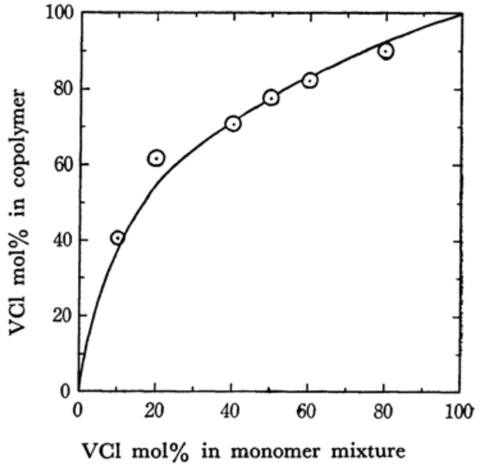

Fig. 5. Copolymer composition curve obtained by the VO(OEt)$_3$-AlEt$_3$ catalyst system at the Al/V molar ratio of 1.5.

The Copolymer Composition. The copolymer composition curve for the copolymerization by the VO(OEt)$_3$/AlEt$_3$ catalyst system is shown in Fig. 5. The compositions of the copolymers obtained by the VO(OEt)$_3$/AlEt$_2$Cl or AlEtCl$_2$ were 86.6 and 85.5 mol% vinyl chloride respectively; these values are comparable to that of 82.3 mol% vinyl chloride obtained for the VO(OEt)$_3$/ AlEt$_3$ catalyst system. Using the Fineman-Ross plot shown in Fig. 6, the monomer reactivity ratios were determined; in Table 2 they are compared with those found in the copolymerization by the Ti(O-*n*-Bu)$_4$/alkylaluminum as well as those obtained by the use of the trialkylboron/peroxide catalyst systems. The monomer reactivity ratios found in the copolymerization catalyzed by the VO(OEt)$_3$/AlEt$_3$ catalyst system are of values

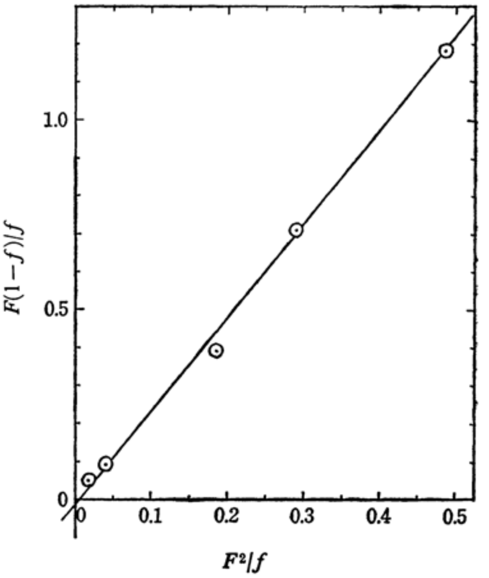

Fig. 6. Determination of r_1 and r_2 by Fineman-Ross method.

intermediate between those found for the Ti(O-n-Bu)$_4$/alkylaluminum-catalyzed and the trialkylboron-catalyzed copolymerizations. The copolymerization catalyzed by the alkyl orthovanadate catalyst system seems to be of a more radical nature than that catalyzed with the alkyl titanate catalyst systems, judging from the monomer reactivity ratios. The copolymerization by the VO(OEt)$_3$/AlEt$_3$ catalyst system was completely inhibited upon the addition of diphenylpycrylhydrazyl in an amount equimolar to VO(OEt)$_3$. However, it seems unclear whether or not this fact directly supports a radical polymerization mechanism for a reason presented in a previous paper.[4]

TABLE 2. COMPARISON OF MONOMER REACTIVITY RATIOS

Catalyst	r_1 (vinyl chloride)	r_2 (ethylene)	Ref.
B(n-Bu)$_3$/t-BHP	3.39	0.03	1
Ti(O-n-Bu)$_4$/ AlEt$_2$Cl	2.03	0.20	4
Ti(O-n-Bu)$_4$/ AlEtCl$_2$/THF	2.70	0.45	3
VO(OEt)$_3$/AlEt$_3$	2.48	0.02	this work

t-BHP: t-butyl hydroperoxide, THF: tetrahydrofuran

Observation of the Catalyst System. VO(OEt)$_3$ reacts with AlEt$_3$, with gas evolution, to form a colored solution in n-heptane; this indicates the occurence of a chemical reaction between the two components. At Al/V molar ratios higher than unity, the dark brown color of the catalyst solution grows deeper as the molar ratio increases. At Al/V molar ratios lower than unity, however, the brown color of the catalyst solution observed soon after it is prepared gradually fades and a green color appears; the solution is essentially green when it has been aged for about one hour. Each color change suggests the presence of a new chemical species and illustrates the complexity of the catalyst-forming reaction. In order to obtained further information concerning the active site-forming reaction, the VO(OEt)$_3$/AlEt$_3$ catalyst system was investigated by means of infrared spectroscopy and gasometry.

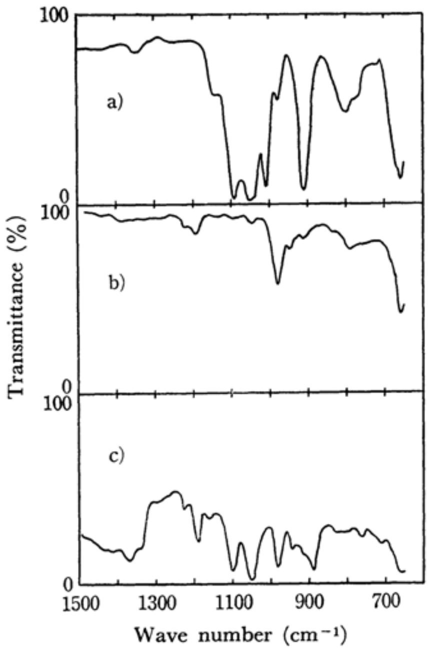

Fig. 7. Infrared spectra of catalyst components.
a) VO(OEt)$_3$ in n-heptane, 40 mmol/l
b) AlEt$_3$ in n-heptane, 40 mmol/l
c) AlEt$_2$ (OEt) in n-heptane, $ca.$ 100 mmol/l.

Figure 7 shows the infrared spectra of both the catalyst components, together with that of diethylaluminum ethoxide, each sample having been prepared as a n-heptane solution. Sekiguchi $et\ al.$[8] have studied the infrared spectrum of alkyl orthovanadates in their crude phase. They have considered the strong absorption at 970 cm^{-1} of VO(O-i-Pr)$_3$, which shifted to a somewhat lower frequency in the case of VO(OEt)$_3$, to be due to the V-O-C structure in the orthovanadates. No such a strong absorption is observed in the spectrum of VO(OEt)$_3$ There are no other available data concerning the infrared spectra of VO(OEt)$_3$ and other alkyl orthovanadates; hence, not even tentative assignments of the absorptions observed in the spectrum under consideration have yet been made.

Figure 8 shows the infrared spectra of the catalyst solutions in n-heptane at various Al/V molar ratios, the concentration of VO(OEt)$_3$ in each solution being adjusted to 40 mmol/l. It is obvious from the spectra shown in Figs. 7 and 8 that, in addition to the absorptions of both VO(OEt)$_3$ and AlEt$_3$, some new absorptions appear in the spectrum of the catalyst solution. For example, a strong and sharp band appears at 890 cm^{-1}. However, it is not clear whether this band arises from the V-O-C structure, which would shift to a lower frequency on complex-formation with AlEt$_3$, or from the Al-O-C structure, which would be formed in the ligand exchange reaction between VO(OEt)$_3$ and AlEt$_3$. A weak absorption at 1155 cm^{-1}, which is not observed in the spectrum of each component, slightly shifts to 1160 cm^{-1} as the Al/V molar ratio of the catalyst system increases. The original strong bands of VO(OEt)$_3$ at 1010, 910, and 800 cm^{-1} quickly disappear as the Al/V molar ratio increases from 0.25 to 1.0, whereas those at 1090 and 1050 cm^{-1} keep their original intensities

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[8] S. Sekiguchi and A. Kurihara, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 2002 (1966).

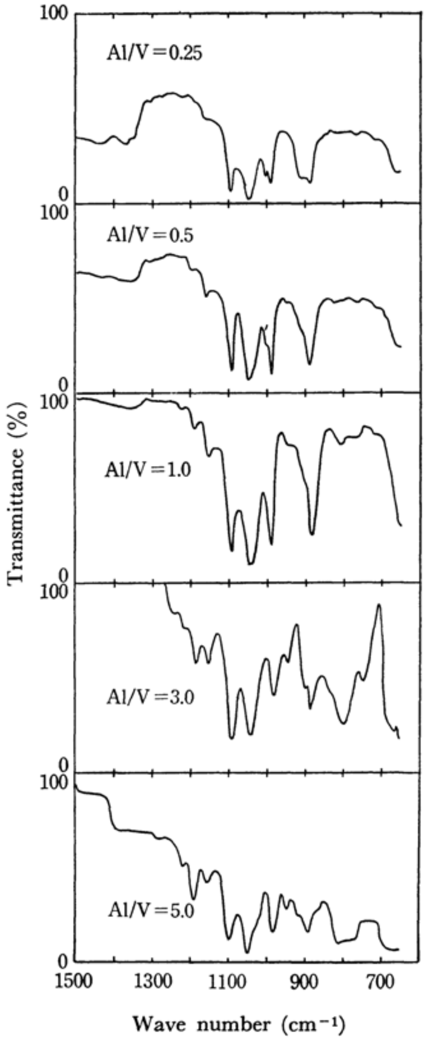

Fig. 8. Infrared spectra of catalyst solutions.

almost independent of the Al/V molar ratio. The absorption at 1090 cm^{-1}, however, shifts to 1100 cm^{-1} as the Al/V molar ratio increases. Other absorptions are observed in the spectrum of the catalyst solution which may be due to $AlEt_3$ present in the solution absorptions at 1225 (weak), 1190(weak), 985(strong), and 800(weak when $Al/V<1.0$, but strong when $Al/V>3.0$) cm^{-1}.

It is obvious that the spectrum of the catalyst solution becomes similar to that of $AlEt_2(OEt)$ as the Al/V molar ratio increases, and that the spectrum at the ratio of 5 is essentially identical with that of $AlEt_2(OEt)$ over the frequency range from 850 to 1300 cm^{-1}. The absorptions at 1160, 1100, and 890 cm^{-1} in the spectrum of $AlEt_2(OEt)$ may be related to the Al–O–C structure in the catalyst solution, judging from the results of a comparison of it with the spectrum of $AlEt_3$. Such absorptions are also observed in the spectrum of the catalyst solution, as has been mentioned previously. In the spectrum of $Al(O\text{-}n\text{-}Bu)_3$ the Al–O–C stretching mode appears at 1080 cm^{-1}. Therefore, one or both of the strong absorptions at 1050 and 1090 cm^{-1}, and the resulting overlapping of the absorptions arising from the two different chemical species, make it impossible to measure quantitatively the concentration of the Al–O–C structure in the catalyst system.

From the results mentioned above, it is, at any rate, obvious that the catalyst system is not a mere mixture of the two components, but that some ligand exchange reaction proceeds, leading to the formation of the Al–O–Et and the V–Et structure in the catalyst system:

$$VO(OEt)_3 + AlEt_3 \rightarrow EtVO(OEt)_2 + AlEt_2(OEt)$$

followed by the reductive dealkylation of the unstable organovanadium compound:

$$EtVO(OEt)_2 \rightarrow VO(OEt)_2 + Et\cdot$$

At higher Al/V molar ratios, ligand exchange and reductive dealkylation may be considered to proceed successively.

Figure 9 shows the amount of gaseous products liberated from the catalyst solution plotted *versus* the reaction time for the reaction of $VO(OEt)_3$ with $AlEt_3$ at 20° C. The gaseous products from the reactions of these two components at the Al/V molar ratio of 1.0 were analyzed after a reaction period of 72 hr; they were found to be composed of ethane and ethylene (1.00 : 0.64), only a small amount of C_4 fractions, and a considerable amount of an unidentified product the peak of which in the gas chromatogram appeared behind the position of that of *n*-heptane. Assuming the unidentified product to be a C_9 fraction resulting from the

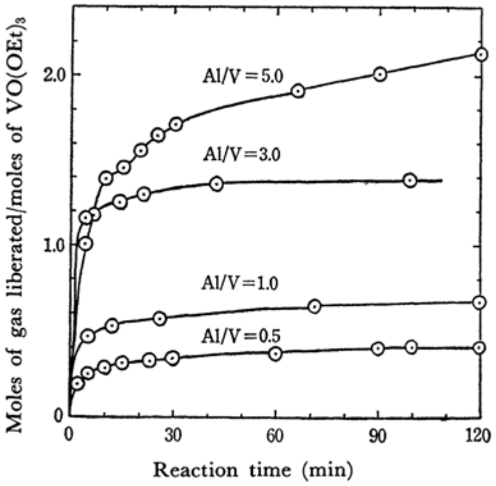

Fig. 9. Reaction of $VO(OEt)_3$ with $AlEt_3$. Experimental conditions: $VO(OEt)_3$, 1.0 mmol, 0.5 mmol for $Al/V=3.0$); solvent, *n*-heptane; volume of catalyst solution, 10 m*l*; reaction temperature, 20°C.

reaction of the ethyl radical with the solvent, its amount could be estimated to be about 20 mol%.

As the reduction of one mole of each organovanadium compound by one valency state leads to the liberation of one mole of gaseous products, it is possible to estimate the average valency state of vanadium in the catalyst system from the results shown in Fig. 9. Figure 10 shows the average valency state of vanadium after the reaction period of one hour plotted against the Al/V molar ratio of the catalyst system. It is obvious that, at the lower Al/V molar ratios, where random copolymers are obtained, the vanadium in the catalyst system is in the valency states higher than four; however, the valency state of vanadium is lower than four at the higher Al/V molar ratios, where polyethylene is mainly obtained in the copolymerization of vinyl chloride with ethylene. This is analogous to what has been considered to hold in the copolymerization of vinyl chloride with ethylene by the $Ti(O\text{-}n\text{-}Bu)_4/AlEtCl_2$ catalyst system[3,9]; the active site producing a random copolymer in this catalyst system may be a titanium complex in a higher valency state, probably a tetravalent one.

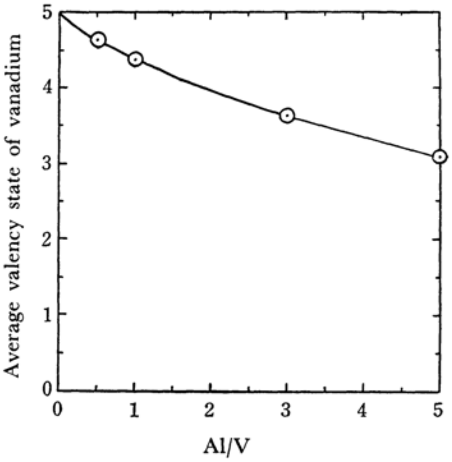

Fig. 10. Average valency state of vanadium *vs.* Al/V molar ratio.

At this stage of invesigation, it can tentatively be considered that the active site in the copolymerization of vinyl chloride with ethylene by the $VO(OEt)_3$/alkylaluminum catalyst systems is an unstable carbon-vanadium bond resulting from the ligand exchange reaction between the two components, as has usually been assumed in polymerizations by Ziegler-Natta catalysts.[10]

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9) N. Yamazaki, K. Sasaki and S. Kambara, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 881 (1965).

10) P. Cossee, *J. Catalysis*, **3**, 80 (1964).