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Copolymerization of Vinyl Chloride with Ethylene by Ziegler-Natta Catalysts

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The copolymerization of vinyl chloride with ethylene by various Ziegler-Natta catalysts was carried out in hydrocarbon solvents at 50°C. On the basis of infrared and NMR spectroscopies of the copolymerization products, it was found that the catalyst systems consisting of $Ti(O\text{-}n\text{-}Bu)_4$ and alkylaluminums can copolymerize vinyl chloride with ethylene, whereas those consisting of VCl_4, $VOCl_3$, $Cr(acac)_3$, $Mn(acac)_3$, or $Co(acac)_3$ and alkylaluminums give polyethylene or a mixture of polyvinyl chloride and polyethylene, and are otherwise inactive. Random copolymers were easily obtained by the use of the $Ti(O\text{-}n\text{-}Bu)_4\text{-}AlEt_2Cl$ and $Ti(O\text{-}n\text{-}Bu)_4\text{-}AlEtCl_2$ catalyst systems. However, with these catalyst systems, polyethylene was obtained, along with a random copolymer, at a high ethylene feed ratio. This fact indicates the existence of two kinds of active sites, responsible to the copolymerization and the ethylene polymerization respectively. The monomer reactivity ratios were found to be r_1(vinyl chloride)$=2.0$ and r_2(ethylene)$=0.2$ for the copolymerization by either the $Ti(O\text{-}n\text{-}Bu)_4\text{-}AlEt_2Cl$ or the $Ti(O\text{-}n\text{-}Bu)_4\text{-}AlEtCl_2$ catalyst system. The monomer reactivity ratios are not in agreement with those found in the conventional radical copolymerization. Though the copolymerization reaction was completely inhibited upon the addition of radical inhibitors, this does not seem to support a radical polymerization mechanism directly.

In a previous paper,[1] the present authors have reported that vinyl chloride can be easily copolymerized with ethylene by trialkylboron-peroxide catalyst systems. Since ethylene is of a far lower reactivity than vinyl chloride in the free radical copolymerization initiated by such catalysts as have been mentioned above, the resultant copolymer is rich in vinyl chloride. On the other hand, since ethylene generally polymerizes in the presence of Ziegler-Natta catalysts, it is very interesting to study the copolymerization of vinyl chloride with ethylene by this type of catalyst, if those active in the polymerization of both monomers are available.

During their studies of the copolymerization of vinyl chloride with ethylene by using various Ziegler-Natta catalysts, the present authors have found that the catalyst systems consisting of $Ti(O\text{-}n\text{-}Bu)_4$ and alkylaluminums can copolymerize these monomers in a manner different from the conventional free radical copolymerization. The copolymerization reactions by these catalyst systems are sensitive to the reaction conditions, the constitution of the reaction product complicatedly varying with the change in the Al/Ti molar ratio of the catalyst system,[2] the structure of the alkylaluminum used,[2] and the presence or the absence of electron-donating substances.[3]

In this paper, the present authors wish to report evidence of copolymer formation as well as the general features of the copolymerization reaction of vinyl chloride with ethylene by the $Ti(O\text{-}n\text{-}Bu)_4$-alkylaluminum catalyst systems within a limited range of Al/Ti molar ratios.

Experimental

Materials. Vinyl chloride supplied by the Chisso Co. was purified by passing it through a column concontaining calcium chloride and then one containing phosphorus 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 a Schlenk apparatus under a pure nitrogen atmosphere. The boiling points of the alkylaluminums were as follows: triethylaluminum, 75—76°C/4 mmHg; diethylaluminum chloride, 75—77°C/7 mmHg; ethylaluminum dichloride, 68—69°C/

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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, International Symposium on Macromolecular Chemistry, Tokyo and Kyoto, 1966, preprint, **I**, p. 132.

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

7 mmHg. Tetra-*n*-butyl titanate supplied by the Mitsubishi Edogawa Chemical Co. was purified by distillation under reduced pressure and was stored as a normal solution in a Schlenk apparatus under a pure nitrogen atmosphere (bp 165—170°C/5 mmHg). Vanadium tetrachloride and vanadyl trichloride were used without further purification. Acetylacetonates of chromium, manganese, and cobalt were prepared and purified according to the published methods. The solvents were purified by shaking them with concentrated sulfuric acid and by distillation over sodium wire.

Polymerization. The reaction vessel was a stainless-steel autoclave equipped with an electro-magnetic agitating device. Unless otherwise mentioned the catalyst system was prepared by mixing a transition metal compound and an alkylaluminum in the absence of the monomers in the autoclave at room temperature under a pure nitrogen atmosphere. Vinyl chloride and ethylene were introduced into the autoclave at −50°C according to the methods described in a previous paper.[1] After the introduction of the monomers had been completed, the autoclave was set in an electric heater and maintained at 50°C for 3 hr. After the reaction time, the residual monomers were expelled as soon as possible and the resultant product was treated with a large amount of methanol containing concentrated hydrochloric acid in order to destroy the catalyst. Then the product was filtered, dried *in vacuo*, and weighed. The crude product thus obtained was purified by dissolving it in tetrahydrofuran and by then pouring the mixture into a large amount of methanol, after which it was filtered and dried *in vacuo*. The composition of the product was calculated from the results of elemental C and Cl analyses. The reduced specific viscosity of the product was measured in a 0.5 g/100 m*l* cyclohexanone solution at 30.0°C. The infrared spectrum of the product was measured with a Hitachi model EPI-S2 infrared spectrometer (KBr disk method). The NMR spectrum of the product 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.

Results and Discussion

The Activity of Various Catalyst Systems. The results of the copolymerization of vinyl chloride with ethylene by various Ziegler-Natta catalysts are summarized in Table 1. Figure 1 shows the infrared spectra of the copolymerization products obtained by some of the catalyst systems shown in Table 1, together with that of a random copolymer obtained in the radical copolymerization. As has been well established, polyvinyl chloride[4] shows an absorption due to the methylene rocking mode at 833 cm^{-1} and polyethylene[5] shows a set of absorptions of the same mode at 730 and 720 cm^{-1} the former being the crystalline band. On the other hand, a random copolymer of vinyl chloride with ethylene shows a characteristic absorption at 750 cm^{-1}; this has been assigned to the methylene rocking mode of a boundary structure in the copolymer chain as follows;[1]

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

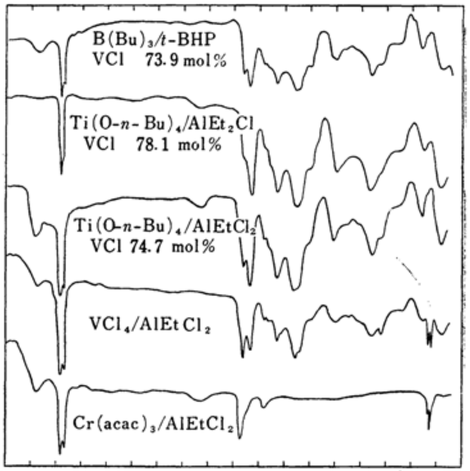

Fig. 1. Infrared spectra of copolymerization products obtained by various catalyst systems.

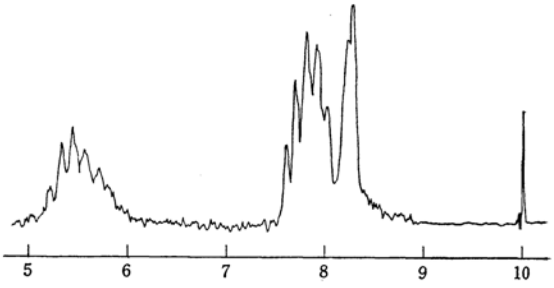

Fig. 2a. NMR spectrum of vinyl chloride-ethylene copolymer obtained by the B(*n*-Bu)$_3$/*t*-BHP catalyst system, containing 88.3 mol% of vinyl chloride.

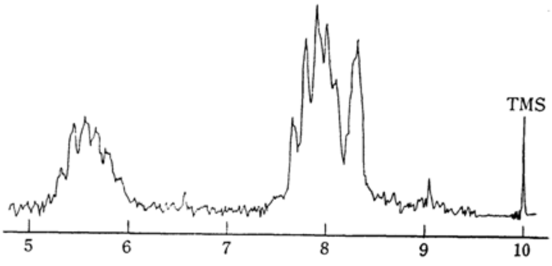

Fig. 2b. NMR spectrum of a vinyl chloride-ethylene copolymer obtained by the Ti(O-*n*-Bu)$_4$-AlEtCl$_2$ catalyst system, vinyl chloride 83.5mol%.

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[4] S. Krimm and C. Y. Liang, *J. Polymer Sci.*, **22**, 95 (1956).

[5] S. Krimm, C. Y. Liang and G. B. B. M. Sutherland, *J. Phys. Chem.*, **25**, 549 (1956).

TABLE 1. RESULTS OF COPOLYMERIZATION BY VARIOUS CATALYSTS

Catalyst (A)	Cocatalyst (B)	B/A[a]	Solvent	VCl* mol% in feed	Yield %	Product
$Ti(O\text{-}n\text{-}Bu)_4$	$AlEt_3$	3.0	heptane	50	trace	PE
$Ti(O\text{-}n\text{-}Bu)_4$	$Al(i\text{-}Bu)_3$	1.8	heptane	50	trace	PE
$Ti(O\text{-}n\text{-}Bu)_4$	$AlEt_2Cl$	3.0	heptane	50	4.6	copolymer[b]
$Ti(O\text{-}n\text{-}Bu)_4$	$AlEtCl_2$	1.8	heptane	70	11.4	copolymer[c]
VCl_4	$Al(O\text{-}n\text{-}Bu)_3$	2.7	hexane	40	0	
VCl_4	$AlEtCl_2$	4.0	hexane	40	6.8	PE
$VOCl_3$	$Al(i\text{-}Bu)_3$	2.3	hexane	40	trace	PVC+PE
$Cr(acac)_3$	$AlEtCl_2$	2.0	benzene	40	2.4	PVC+PE
$Mn(acac)_3$	$AlEtCl_2$	3.0	hexane	40	trace	PVC+PE
$Co(acac)_3$	$AlEtCl_2$	3.0	hexane	40	trace	PVC+PE

Experimental conditions: vinyl chloride+ethylene, 0.5 mol; catalyst, 2.0 mmol; solvent, 50 m*l*; polymerization temperature, 50°C; polymerization time, 3 hr.

* VCl=vinyl chlcride

a) Expressed in molar ratio; b) VCl mol%, 78.1; c) VCl mol%, 74.7

TABLE 2. INFLUENCE OF MIXING ORDER

Mixing order	Al/Ti mol ratio	Temp. °C	Yield %	η_{sp}/C	VCl mol% in product
VCl-(Al, Ti, E)	5.0	50	0	—	violet liquid
VCl-(Al, Ti, E)	1.8	25	0	—	violet liquid
Ti-VCl-(Al, E)	1.8	50	5.2	0.198	70.5
VCl-Ti-Al-E	1.8	−50	3.9	0.204	66.3
Ti-Al-VCl-E	1.8	−50	6.0	0.167	72.9

Experimental conditions: vinyl chloride, 0.2 mol; ethylene, 0.3 mol; $Ti(O\text{-}n\text{-}Bu)_4$, 2.0 mmol; $AlEtCl_2$, varied; solvent, *n*-hexane 30 m*l*; polymerization temperature, 50°C.; polymerization time, 3 hr.

VCl=vinyl chloride, E=ethylene, Ti=$Ti(O\text{-}n\text{-}Bu)_4$, Al=$AlEtCl_2$

Components indicated in brackets were added in the same time.

Therefore, the absorptions appearing in these regions in the infrared spectra of the copolymerization products provide a useful criterion for their characterization.

Thus, from the results shown in Table 1 and Fig. 1, it follows that the catalyst systems consisting of $Ti(O\text{-}n\text{-}Bu)_4$ and $AlEt_2Cl$ or $AlEtCl_2$ produce copolymers, whereas those consisting of transition metal compounds of V–VIII groups and alkylaluminum, shown in Table 1, give polyethylene or a mixture of polyvinyl chloride and polyethylene, and are otherwise inactive. Figure 2 shows the NMR spectrum of the product obtained by the $Ti(O\text{-}n\text{-}Bu)_4\text{-}AlEtCl_2$ catalyst system, together with that obtained in the free radical copolymerization, the two samples being of almost the same composition. Two multiplets, centered at 5.5 τ and 7.9 τ respectively, are observed in either the spectrum of polyvinyl chloride or that of the copolymerization product. On the other hand, only a singlet at 8.3 τ is observed in the spectrum of the copolymerization product. From the fact that the methylene proton resonance of polyvinyl chloride appears at 7.8—8.0 τ while that of polyethylene appears at 8.7 τ, the above-observed resonance of the copolymerization product at 8.3 τ can be assigned to protons in the boundary structure, as has been described above. These observations on the NMR spectrum of the copolymerization product also indicate that the product consists of a true copolymer.

It is interesting to note that, even when combined with $Ti(O\text{-}n\text{-}Bu)_4$, alkylaluminums containing no chlorine atom, such as triethylaluminum and tri-*i*-butyl aluminum, are inactive in the copolymerization. This seems to suggest that the chlorine atom in the alkylaluminum plays an important role in the active-site formation in the copolymerization reaction. The above observations are in agreement with what has been found by Yamazaki and his coworkers in the polymerization of vinyl chloride⁶⁾ as well as in the copolymerization of vinyl chloride with propylene⁷⁾ by the $Ti(O\text{-}n\text{-}Bu)_4$-alkylaluminum catalysts.

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

7) N. Yamazaki and M. Aridomi, International Symposium on Macromolecular Chemistry, Tokyo and Kyoto, 1966, preprint, **I**, p. 128.

The Influence of the Mixing Order of the Reactants. Table 2. shows the influence of the mixing order of the catalyst components and the monomers. When vinyl chloride and $AlEtCl_2$ were brought into contact prior to the addition of the other components, a violet liquid was obtained instead of the copolymer. On observing the reaction of vinyl chloride with $AlEtCl_2$, it becomes clear that this liquid was a reaction product of them. Except for the mixing order mentioned above, the mixing orders of the catalyst components and the presence or the absence of the monomers at the time of the catalyst preparation do not seem to have any significant influence upon the copolymerization reaction.

The Influence of the Monomer Feed Ratio. As has been briefly described in the introductory section, the copolymerization catalyzed by the $Ti(O\text{-}n\text{-}Bu)_4$-alkylaluminum catalyst systems are remarkably subjected to the change in the Al/Ti molar ratios of the catalyst systems. To avoid complications, henceforth, the arguments will be limited to the copolymerizations at relatively low Al/Ti molar ratios where random copolymers are obtained. A detailed discussion of the influence of the Al/Ti molar ratio on the copolymerization by the catalyst systems under consideration will be given elsewhere.

Figures 3 and 4 show the infrared spectra of the copolymerization products obtained by the $Ti(O\text{-}n\text{-}Bu)_4$-$AlEt_2Cl$ system and the $Ti(O\text{-}n\text{-}Bu)_4$-$AlEtCl_2$ catalyst system at various monomer feed ratios. It may easily be seen that a copolymer comes to be contaminated with polyethylene as the ethylene content of the monomer mixture increases. This contamination of a copolymer with polyethylene begins at a 65 mol% vinyl chloride feed with the $Ti(O\text{-}n\text{-}Bu)_4$-$AlEt_2Cl$ catalyst system, and at a 40 mol% vinyl chloride feed with the $Ti(O\text{-}n\text{-}Bu)_4$-$AlEtCl_2$ catalyst system. Above these critical vinyl chloride feed ratios, no ethylene oligomers were detected in the reaction medium by gas chromatography (column, tricresyl phosphate; column temperature, 100°C; flow rate of He, 39 ml/min). Further on evaporating the solvent, only traces of viscous low-molecular weight-copolymers were obtained. Accordingly, any active site responsible to the ethylene polymerization does not seem to operate above the critical vinyl chloride feed ratios.

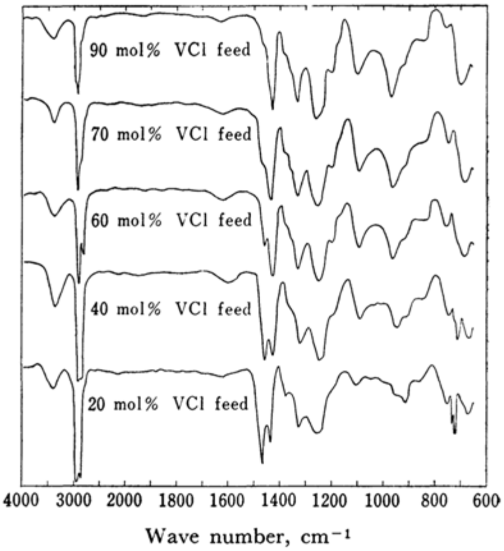

Fig. 4. Infrared spectra of the copolymerization product obtained by the $Ti(O\text{-}n\text{-}Bu)_4$-$AlEtCl_2$ catalyst system at various VCl feed ratio.

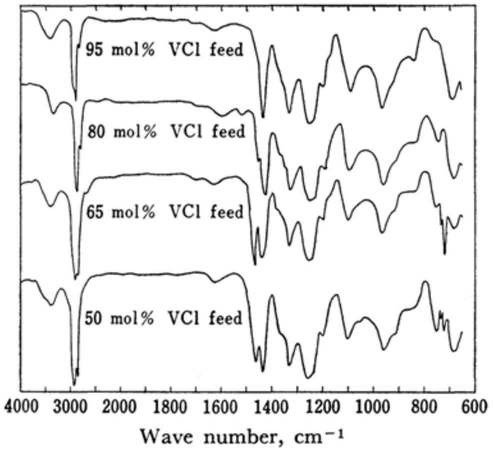

Fig. 3. Infrared spectra of the copolymerization product obtained by the $Ti(O\text{-}n\text{-}Bu)_4$-$AlEt_2Cl$ catalyst system at various VCl feed ratio.

These facts seem to suggest that, in the copolymerization by these catalyst systems, at least two kinds of active sites are present, one of them being

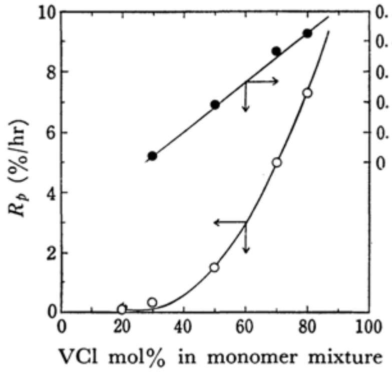

Fig. 5. Copolymerization rate and the reduced specific viscosity of the product in the copolymerization by the $Ti(O\text{-}n\text{-}Bu)_4$-$AlEt_2Cl$ catalyst system.
vinyl chloride+ethylene=0.5 mol,
$Ti(O\text{-}n\text{-}Bu)_4$=2.0 mmol,
n-heptane=50 ml, 50°C.

active in the copolymerization and the other active only in the ethylene polymerization. A competition for the incorporation of the ethylene monomer may take place between the two kinds of active sites, the one for the copolymerization being more active toward ethylene than the other. Hence, the copolymer is obtained exclusively at a high vinyl chloride feed ratio, and then polyethylene begins to be formed along with the copolymer at a relatively low vinyl chloride feed ratio.

The rate of the copolymerization and the reduced specific viscosity of the copolymer decrease with the increasing ethylene feed ratio in the copolymerization by either catalyst system, as is shown in Figs. 5 and 6. These tendencies are analogous to what has been found in the radical copolymerization initiated by the trialkylboron-peroxide catalyst systems.[1] This indicates that vinyl chloride is more active than ethylene in the Ziegler-Natta copolymerization under consideration also.

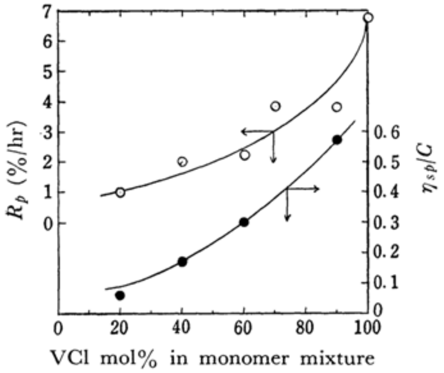

Fig. 6. Copolymerization rate and the reduced specific viscosity of the product in the copolymerization by the Ti(O-n-Bu)$_4$-AlEtCl$_2$ catalyst system.
vinyl chloride + ethylene = 0.5 mol,
Ti(O-n-Bu)$_4$ = 2.0 mmol, AlEtCl$_2$ = 3.5 mmol,
n-heptane = 50 ml, 50°C.

The Copolymer Composition. The copolymres with a high vinyl chloride content were white powdery materials, whereas those rich in ethylene had an elastomeric appearance. Since the copolymers obtained in this study were not colored to any extent, and since their compositions, as calculated from the elemental C and Cl analyses, were in good agreement with each other, it seems unlikely that any side reaction such as the dehydrochlorination of the copolymer occur during the copolymerization reactions.

The copolymer composition curve for the copolymerization by the Ti(O-n-Bu)$_4$-AlEt$_2$Cl and Ti(O-n-Bu)$_4$-AlEtCl$_2$ catalyst systems is shown in Fig. 7, together with that for the radical copolymerization initiated by the tri-n-butylboron/t-butyl hydroperoxide catalyst system.[1] When the copolymer was contaminated with polyethylene, the copolymer was separated by the extraction using tetrahydrofuran, and the pure copolymer thus obtained was analyzed to determine its composition. Since the conversion was low (below 10%), the above procedure will not lead to an erroneous result. The copolymer composition depends only on the monomer feed ratio, and not on whether the Ti(O-n-Bu)$_4$-AlEt$_2$Cl or the Ti(O-n-Bu)$_4$-AlEtCl$_2$ catalyst system is used.

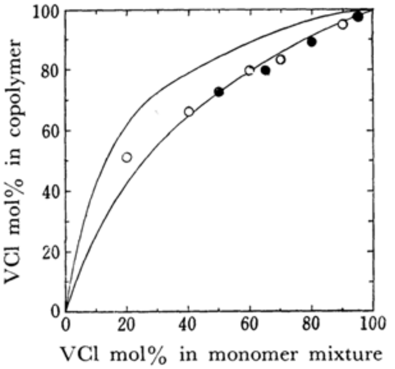

Fig. 7. The copolymer composition curve for the copolymerization by the Ti(O-n-Bu)$_4$-AlEt$_2$Cl and -AlEtCl$_2$ catalyst systems.
white circle: experimental points for the Ti(O-n-Bu)$_4$-AlEt$_2$Cl
black circle: experimental points for the Ti(O-n-Bu)$_4$-AlEtCl$_2$
line without experimental points: for the radical copolymerization initiated by the B(Bu)$_3$/t-BHP catalyst system

Using the Fineman-Ross plot shown in Fig. 8, the monomer reactivity ratios were determined. They are compared with the monomer reactivity ratios found in the conventional radical copolymerization in Table 3. The monomer reactivity

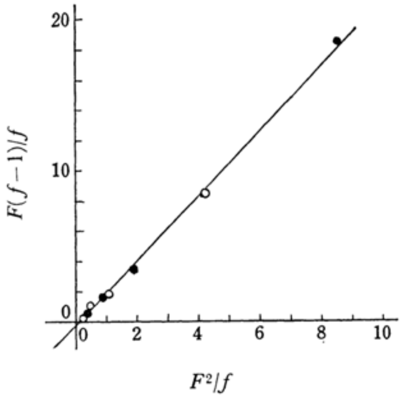

Fig. 8. Evaluation of r_1 and r_2 by Fineman-Ross method.
white circle: experimental points for the Ti(O-n-Bu)$_4$-AlEt$_2$Cl
black circle: experimental points for the Ti(O-n-Bu)$_4$-AlEtCl$_2$

TABLE 3. COMPARISON OF MONOMER REACTIVITY RATIOS

Catalyst	r_1(vinyl chloride)	r_2(ethylene)	Worker
AIBN	3.60	0.24	Burkhalt *et al.*[8]
$B(n\text{-}Bu)_3/t\text{-}BHP$	4.18	0.05	Misono *et al.*[1]
$Ti(O\text{-}n\text{-}Bu)_4/AlEt_2Cl$	2.03	0.20	this work
$Ti(O\text{-}n\text{-}Bu)_4/AlEt_2Cl$	2.03	0.20	this work

AIBN = α, α-azobisisobutyronitrile, *t*-BHP = *t*-butyl hydroperoxide

ratios found in this study are not in agreement with those found in the radical copolymerization. As can be seen from Fig. 7, the copolymers obtained by using the $Ti(O\text{-}n\text{-}Bu)_4$-alkylaluminum catalyst systems are considerably richer in ethylene than those obtained in the radical copolymerization. Ethylene has been known to be more susceptible to coordination polymerization than a free radical. The copolymerization by the $Ti(O\text{-}n\text{-}Bu)_4\text{-}AlEtCl_4$ catalyst system was completely inhibited upon the addition of a typical radical inhibitor, hydroquinone or diphenylpicrylhydrazyl, the amounts of the inhibitor added being, respectively, 2.4 and 1.5 molar equivalents of the $Ti(O\text{-}n\text{-}Bu)_4$ of the catalysts system. In spite of this fact, it remains unclear whether or not this directly supports a radical polymerization mechanism, because hydroquinone or diphenylpicrylhydrazyl is considered to react with the catalyst components or with the catalyst system itself to inactivate or destroy them.

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8) R. D. Burkhalt and N. L. Zutty, *J. Polymer Sci.*, **A1**, 1137 (1963).