Macromolecules 1992, 25, 2820–2827

Sequence and Branching Distribution of Ethylene/1-Butene Copolymers Prepared with a Soluble Vanadium-Based Ziegler–Natta Catalyst

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Received October 16, 1991; Revised Manuscript Received February 3, 1992

ABSTRACT: The theoretical relations between ^{13}C NMR line intensities and the triad distributions of ethylene/1-butene copolymer containing 1-butene units incorporated by primary and secondary insertion (B, B*) were derived. On the basis of these relations, the triad distributions of ethylene/1-butene copolymer prepared with a soluble vanadium-based Ziegler–Natta catalytic system $VOCl_3/Al_2(C_2H_5)_3Cl_3$ were determined by ^{13}C NMR measurements. Conditional probabilities (P_{EE}, P_{EB}, P_{EB^*}, P_{BE}, P_{BB}, P_{BB^*}, P_{B^*E}, P_{B^*B}, $P_{B^*B^*}$), mole fractions of comonomers (E, B, B^*), and products of reactivity ratios ($r_{EB}r_{BE}$, $r_{EB^*}r_{B^*E}$) were calculated from the triad distributions observed. The analysis of these values suggests that the copolymer has an alternating-type sequence distribution and 80% of 1-butene units in copolymer follow the primary insertion. It is also suggested that this catalyst has one type of active site. The latter result was confirmed by comparison of the branching distribution of copolymer determined by temperature-rising elution fractionation (TREF) with that of copolymer model calculated theoretically on the assumption that the catalyst has only one type of active site. These results are distinct from those of a heterogeneous titanium-based SiO_2-supported catalytic system of $TiCl_4/Al(C_2H_5)_3$. The latter catalyst has multiple active sites which form copolymers having 1-butene units incorporated by primary insertion and a nearly Bernoullian sequence distribution. It is suggested that the simultaneous use of ^{13}C NMR and TREF can enlighten the copolymer structure and the nature of the active sites.

Introduction

A number of studies on sequence distributions in ethylene/1-butene copolymers prepared with both soluble and heterogeneous Ziegler–Natta catalysts have been carried out by means of ^{13}C NMR studies. Sequence distributions are of particular importance in ethylene/1-butene copolymers since crystallinity which results from long ethylene sequences affects the mechanical performance of the final products.

In the case of ^{13}C NMR analysis of copolymers prepared with Ziegler–Natta catalysts, it is necessary to consider the nature of the active sites. If the catalyst has multiple active sites whose physical properties such as oxidation state, electronic environment, and steric environment are different from each other and the catalyst produces copolymers with broad branching distribution, we have to use fractionation to separate the polymer chains corresponding to each active site. For instance, we suggested in a previous paper that a heterogeneous titanium-based Ziegler–Natta catalyst has multiple active sites, and most publications dealing with copolymers prepared with this catalytic system without fractionation do not tell us the true character of each active site.[1] Cozewith also showed that ^{13}C NMR is not a sensitive technique for unequivocally establishing the nature of the active sites, and additional confirmation by molecular weight distribution or polymer branching distribution is highly desirable in the case of ethylene/propylene copolymer prepared with a heterogeneous catalyst.[2]

Recently, a temperature-rising elution fractionation technique (TREF) has become a powerful tool for the purpose of determining branching distribution.[3,4] This technique achieves fractionation on the basis of crystallizability, which is shown to be predominantly influenced by short chain branching and very little influenced by molecular weight in the standard high polymer range. By means of simultaneous use of ^{13}C NMR and TREF, insights could be obtained into the nature of the active sites of the catalysts. If the catalyst has one type of active site, the ^{13}C NMR method could be used without fractionation.

A soluble vanadium-based catalyst is very important to produce ethylene/propylene rubber (EPR). 1-Butene is also used as a comonomer in this catalytic system. Cozewith and Ver Strate made a very important contribution to this field using a kinetic method.[5] However, the kinetic method does not provide as clear insights into the nature of active sites as the ^{13}C NMR method. There are also publications dealing with copolymers prepared with a soluble vanadium-based catalyst by means of ^{13}C NMR. For instance, Smith determined the sequence distribution of ethylene/propylene copolymers prepared with $VOCl_3/Al_2(C_2H_5)_3Cl_3$; however, he used unfractionated copolymers without taking into account the nature of the active sites.[6] Ohgisawa determined the sequence distribution of the same copolymers prepared with tris(2-methyl-1,3-butanedionate)vanadium/$Al(C_2H_5)_2Cl$; however, she did not use the fractionation technique either.[7] Ray et al. determined the sequence distributions of ethylene/1-butene copolymers prepared with both a soluble vanadium-based and a heterogeneous titanium-based catalyst, but they did not

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Table I
Fractionation of the Ethylene/1-Butene Copolymer (Number-Average Molecular Weight $\bar{M}_n$ = 36 000) by Successive Extraction with Solvent

no.	fraction[a]	wt fraction, %
F-1	IPE sol (20 °C)	1.4
F-2	IPE insol (20 °C)/n-C_6 sol (20 °C)	2.1
F-3	n-C_6 insol (20 °C)/n-C_6 sol (bp)	96.5

[a] IPE, diisopropyl ether; n-C_6, $CH_3(CH_2)_4CH_3$.

use the fractionation technique.[8] Chûjô et al. proposed that a heterogeneous titanium-based catalyst has two active sites of which one site is more reactive toward ethylene and the other site is more reactive to 1-butene; however, they also did not use the fractionation technique.[9,10]

In the present study, the ethylene/1-butene copolymer prepared with a soluble vanadium-based catalytic system $VOCl_3/Al_2(C_2H_5)_3Cl_3$ was examined by ^{13}C NMR and TREF, and the sequence distribution was determined. The nature of the active sites was also discussed in more detail. In particular, the difference between a soluble vanadium-based and a heterogeneous titanium-based catalyst was discussed.

Experimental Section

The ethylene/1-butene copolymers were produced by a soluble vanadium-based and a heterogeneous titanium-based catalyst. In the case of the vanadium-based catalyst, the copolymer was continuously produced in a 2-L reactor using $VOCl_3/Al_2(C_2H_5)_3Cl_3$. The copolymerization was performed at 20 °C. In the case of the titanium-based catalyst, the copolymer was produced in a pilot plant reactor using a SiO_2-supported catalytic system of $TiCl_4/Al(C_2H_5)_3$. Copolymerization was performed at 80 °C. Hydrogen was used as the chain-transfer agent in both cases.

The copolymer prepared with the soluble vanadium-based catalyst was fractionated by successive solvent extractions using diisopropyl ether (IPE) at 20 °C, n-hexane at 20 °C, and boiling n-hexane. Three fractions were obtained by this fractionation.

The ^{13}C NMR spectra were recorded on a JEOL JNM FX-400 spectrometer at 100.4 MHz. The instrument conditions were as follows: pulse angle, 45°; pulse delay, 9.18 s; acquisition time, 0.82 s; spectral width, 20 kHz; number of data points per spectrum, 32K; double-precision arithmetic. Sample measurements were taken at 130 °C with broad-band decoupling. Polymer solutions for the ^{13}C NMR measurements were prepared in o-dichlorobenzene (ODCB), with concentrations of about 8 g/100 cm^3. The observed chemical shifts were referenced to an internal hexamethyldisiloxane (HMDS) standard and corrected to tetramethylsilane (TMS) by adding 1.95 ppm. The intensity measurements were made from integrated areas by using the spectrometer's integration software.

The number-average molecular weights $\bar{M}_n$ of the samples were determined by gel permeation chromatography (GPC). The chromatogram was recorded at 135 °C on a Waters ALC/GPC 150C instrument using ODCB as the solvent. The solution concentration was 0.15 g/100 cm^3.

The branching distributions of the copolymers were determined by a TREF system constructed in our laboratory based on the system reported by Wild et al.[3] and Usami et al.[4] ODCB was used as the elution solvent.

Results and Discussion

Fractionation of Copolymer. The results of the fractionation of the ethylene/1-butene copolymer prepared with a soluble vanadium-based catalytic system $VOCl_3/Al_2(C_2H_5)_3Cl_3$ are shown in Table I. The weight fraction of fraction three (F-3) is 96.5%. Apparently this copolymer exhibits a narrow distribution in terms of branching, in other words, a narrow compositional distribution. The result mentioned above is completely different from that of a heterogeneous titanium-based Ziegler–Natta catalyst.[1]

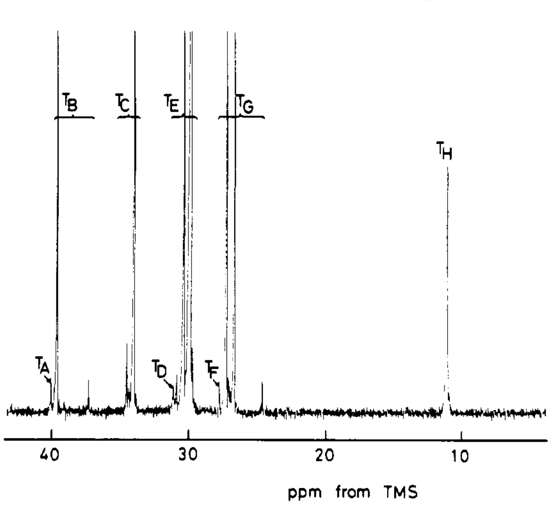
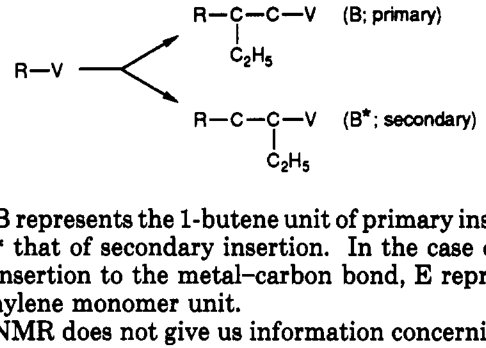


Figure 1. ^{13}C NMR spectra at 100.4 MHz of ethylene/1-butene copolymer prepared with a soluble vanadium-based catalytic system $VOCl_3/Al_2(C_2H_5)_3Cl_3$.

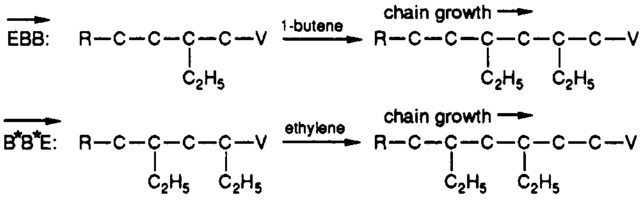
Sequence Distribution of Copolymer Prepared with a Soluble Vanadium-Based Catalytic System $VOCl_3/Al_2(C_2H_5)_3Cl_3$. In Figure 1 are shown ^{13}C NMR spectra of ethylene/1-butene copolymer prepared with the catalytic system $VOCl_3/Al_2(C_2H_5)_3Cl_3$. We used the original copolymer for ^{13}C NMR measurment since the results of fractionation show that this copolymer has a very narrow compositional distribution. The validity of using the original copolymer in this case will be justified later.

The triad distributions observed were determined according to Hsieh and Randall's method[11] and Smith's method.[6] With regard to 1-butene insertion to the metal–carbon bond, we have to consider the primary and secondary insertion:



Thus, B represents the 1-butene unit of primary insertion and B* that of secondary insertion. In the case of ethylene insertion to the metal–carbon bond, E represents the ethylene monomer unit.

^{13}C NMR does not give us information concerning the direction of the growth reaction or the mode of the 1-butene insertion. However, we need to specify the direction of the growth reaction in discussing the kinetic parameters. This will be done by placing an arrow over the multad symbol to signify that the polymerization producing the multad proceeded from left to right. For instance, a triad such as EBB (polymerization direction unspecified) can be formed in two different ways:



On the basis of the above discussion, each triad distribution is represented as follows:

$$\text{EEE} = \overrightarrow{\text{EEE}} \tag{1}$$

$$\text{BEE} = \overrightarrow{\text{BEE}} + \overrightarrow{\text{EEB*}} \tag{2}$$

$$\text{EEB} = \overrightarrow{\text{EEB}} + \overrightarrow{\text{B*EE}} \tag{3}$$

$$\text{EBE} = \overrightarrow{\text{EBE}} + \overrightarrow{\text{EB*E}} \tag{4}$$

$$\text{BBE} = \overrightarrow{\text{BBE}} + \overrightarrow{\text{EB*B*}} \tag{5}$$

$$\text{EBB} = \overrightarrow{\text{EBB}} + \overrightarrow{\text{B*B*E}} \tag{6}$$

$$\text{BEB} = \overrightarrow{\text{BEB}} + \overrightarrow{\text{B*EB*}} \tag{7}$$

$$\text{BEB*} = \overrightarrow{\text{BEB*}} \tag{8}$$

$$\text{B*EB} = \overrightarrow{\text{B*EB}} \tag{9}$$

$$\text{EBB*} = \overrightarrow{\text{EBB*}} + \overrightarrow{\text{BB*E}} \tag{10}$$

Here, BBB, EB*B, BB*B, and BBB* are taken to be zero, since B*B and triad linkages of 1-butene are not found in the ^{13}C NMR spectrum.

^{13}C NMR also cannot distinguish between BEE and EEB or BBE and EBB. Thus, ^{13}C NMR only gives information on the following triads:

$$[\text{EEE}] = \text{EEE} \tag{11}$$

$$[\text{BEE}] = \text{BEE} + \text{EEB} \tag{12}$$

$$[\text{EBE}] = \text{EBE} \tag{13}$$

$$[\text{BBE}] = \text{BBE} + \text{EBB} \tag{14}$$

$$[\text{BEB}] = \text{BEB} \tag{15}$$

$$[\text{BEB*}] = \text{BEB*} \tag{16}$$

$$[\text{B*EB}] = \text{B*EB} \tag{17}$$

$$[\text{EBB*}] = \text{EBB*} \tag{18}$$

Brackets indicate the sequence mole fractions determined directly by ^{13}C NMR.

The relations between diads and triads are

$$\begin{aligned}\text{EE} &= \overrightarrow{\text{EE}} \\ &= \text{EEE} + {}^{1}\!/_{2}(\text{EEB} + \text{BEE})\end{aligned} \tag{19}$$

$$\begin{aligned}\text{EB} &= \overrightarrow{\text{EB}} + \overrightarrow{\text{B*E}} \\ &= \text{EEB} + \text{BEB} + 2\text{B*EB} \\ &= \text{EBE} + \text{EBB} + \text{EB*B}\end{aligned} \tag{20}$$

$$\begin{aligned}\text{BE} &= \overrightarrow{\text{BE}} + \overrightarrow{\text{EB*}} \\ &= \text{BEE} + \text{BEB} + 2\text{BEB*} \\ &= \text{EBE} + \text{BBE}\end{aligned} \tag{21}$$

$$\begin{aligned}\text{BB} &= \overrightarrow{\text{BB}} + \overrightarrow{\text{B*B*}} \\ &= \text{EBB} \\ &= \text{BBE}\end{aligned} \tag{22}$$

$$\begin{aligned}\text{BB*} &= \overrightarrow{\text{BB*}} \\ &= {}^{1}\!/_{2}\text{EBB*}\end{aligned} \tag{23}$$

Moreover

$$\begin{aligned}[\text{EE}] &= \text{EE} \\ &= [\text{EEE}] + {}^{1}\!/_{2}[\text{EEB}]\end{aligned} \tag{24}$$

$$\begin{aligned}[\text{EB}] &= \text{EB} + \text{BE} \\ &= [\text{EEB}] + 2[\text{BEB}] + 2[\text{B*EB}] + 2[\text{BEB*}] \\ &= 2[\text{EBE}] + [\text{BBE}] + {}^{1}\!/_{2}[\text{EBB*}]\end{aligned} \tag{25}$$

$$\begin{aligned}[\text{BB}] &= \text{BB} \\ &= {}^{1}\!/_{2}[\text{EBB}]\end{aligned} \tag{26}$$

$$\begin{aligned}[\text{BB*}] &= \text{BB*} \\ &= {}^{1}\!/_{2}[\text{EBB*}]\end{aligned} \tag{27}$$

The relations between monads and diads are

$$\begin{aligned}[\text{E}] &= \overrightarrow{\text{E}} \\ &= \text{EE} + {}^{1}\!/_{2}(\text{EB} + \text{BE}) \\ &= [\text{EE}] + {}^{1}\!/_{2}[\text{EB}]\end{aligned} \tag{28}$$

$$\begin{aligned}[\text{B}] &= \overrightarrow{\text{B}} + \overrightarrow{\text{B*}} \\ &= {}^{1}\!/_{2}(\text{EB} + \text{BE}) + \text{BB} + \text{BB*} \\ &= \text{BB} + \text{EB}\end{aligned} \tag{29}$$

The triad distributions are calculated from ^{13}C NMR according to Hsieh and Randall's method.[11] They calculated the triad distributions in the case of no secondary insertion, namely no existence of B* unit. However, since the copolymer prepared with a soluble vanadium-based catalyst has B* unit attributed to the secondary insertion, we have to derive new equations as follows. The spectral region is divided into eight areas as shown in Figure 1. T is the total intensity of each region. The relationships between the total intensity of each region and triads are

$$T_{\text{A}} = k([\text{EBB*}] + 2[\text{B*EB}]) \tag{30}$$

$$T_{\text{B}} = k({}^{3}\!/_{2}[\text{BBE}] + [\text{EBE}]) \tag{31}$$

$$T_{\text{C}} = k([\text{BBE}] + 2[\text{EBE}] + [\text{EBB*}] + 2[\text{B*EB}]) \tag{32}$$

$$T_{\text{D}} = k([\text{EBB*}] + 2[\text{B*EB}]) \tag{33}$$

$$T_{\text{E}} = k(2[\text{EEE}] + {}^{1}\!/_{2}[\text{BEE}]) \tag{34}$$

$$T_{\text{F}} = k(2[\text{BEB*}] + 2[\text{B*EEB}]) \tag{35}$$

$$T_{\text{G}} = k(2[\text{BBE}] + 3[\text{EBE}] - [\text{BEB}] + [\text{EBB*}] + 2[\text{B*EB}]) \tag{36}$$

$$T_{\text{H}} = k[\text{B}] \tag{37}$$

where k is the NMR constant, which can be removed later through normalization. From these equations, we can get

Table II
Calculated and Observed Triad Distributions (E = Ethylene; B, B* = 1-Butene)

	calcd		
triad	first-order Markovian	Bernoullian	obsd
EEE	0.707	0.726	0.707
BEE	0.086	0.082	0.181
EEB	0.091	0.082	
EBE	0.096	0.082	0.094
BBE	0.003	0.007	0.005
EBB	0.003	0.007	
BEB	0.007	0.007	0.007
BEB*	0.001_7	0.001	0.006
B*EB	0.001_8	0.001	
EBB*	0.002_5	0.002	
EB*B	0.000	0.002	0.000
BBB	0.000	0.001	0.000

the triad distributions k[EEE], k[BEE], k[EBE], k[BBE], and k[BEB]:

$$k[\mathrm{EEE}] = {}^1/_6(T_\mathrm{A} + T_\mathrm{B} + T_\mathrm{C} + 3T_\mathrm{E} - 2T_\mathrm{G} + \beta\beta(\mathrm{BEB})) = {}^1/_{16}(6T_\mathrm{A} + 6T_\mathrm{B} - 4T_\mathrm{C} + 8T_\mathrm{E} - 2T_\mathrm{G} + 6\beta\beta(\mathrm{BEB}) - 5\mathrm{CH}(\mathrm{BBE})) \quad (38)$$

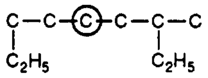
$$k[\mathrm{BEE}] = {}^2/_3(-T_\mathrm{A} - T_\mathrm{B} - T_\mathrm{C} + 2T_\mathrm{G} - \beta\beta(\mathrm{BEB})) = {}^1/_4(-6T_\mathrm{A} - 6T_\mathrm{B} + 4T_\mathrm{C} + 2T_\mathrm{G} + 5\mathrm{CH}(\mathrm{BBE}) - 6\beta\beta(\mathrm{BEB})) \quad (39)$$

$$k[\mathrm{EBE}] = {}^1/_3(-2T_\mathrm{A} - 2T_\mathrm{B} + T_\mathrm{C} + T_\mathrm{G} + \beta\beta(\mathrm{BEB})) = {}^1/_8(-6T_\mathrm{A} - 6T_\mathrm{B} + 4T_\mathrm{C} + 2\beta\beta(\mathrm{BEB}) + \mathrm{CH}(\mathrm{BBE})) + 2T_\mathrm{G} \quad (40)$$

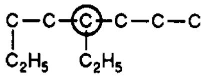
$$k[\mathrm{BBE}] = {}^2/_3(T_\mathrm{A} + T_\mathrm{B} - 2T_\mathrm{C} + T_\mathrm{G} + \beta\beta(\mathrm{BEB})) \quad (41)$$

$$k[\mathrm{BEB}] = \beta\beta(\mathrm{BEB}) \quad (42)$$

Here, $\beta\beta$(BEB) and CH(BBE) are the intensities for the resonances assigned to the circled carbons of



and



(polymerization direction unspecified), respectively. Concerning k[EBB*], k[B*EB], and k[BEB*], we cannot decide these values from ^{13}C NMR.

The sum of triad distributions provides the normalization factor which leads to final expressions for the triad distributions in terms of mole fractions:

$$\mathrm{TTA} = \text{total triad area} = k([\mathrm{E}] + [\mathrm{B}]) = k([\mathrm{EEE}] + [\mathrm{BEE}] + [\mathrm{EBE}] + [\mathrm{BBE}] + [\mathrm{BEB}] + [\mathrm{BEB^*}] + [\mathrm{B^*EB}] + [\mathrm{EBB^*}]) \quad (43)$$

Since it is not possible to calculate k([BEB*] + [B*EB] + [EBB*]), an approximation should be made to obtain the value of TTA as follows:

$$\mathrm{TTA} = k([\mathrm{EEE}] + [\mathrm{BEE}] + [\mathrm{EBE}] + [\mathrm{BBE}] + [\mathrm{BEB}] + 2[\mathrm{B^*EB}] + [\mathrm{EBB^*}]) \quad (44)$$

Obviously, the difference between [BEB*] and [B*EB] is negligible compared to the TTA because [BEB*] and [B*EB] are very small. The observed triad distributions calculated from the equations mentioned above are given in Table II.

To determine whether the polymerization follows the first-order Markovian process with respect to the monomeric unit or not, the triad distributions are calculated as

$$\mathrm{EEE} = EP_\mathrm{EE}{}^2 \quad (45)$$

$$\mathrm{BEE} = BP_\mathrm{BE}P_\mathrm{EE} + EP_\mathrm{EE}P_\mathrm{EB^*} \quad (46)$$

$$\mathrm{EEB} = EP_\mathrm{EE}P_\mathrm{EB} + B^*P_\mathrm{B^*E}P_\mathrm{EE} \quad (47)$$

$$\mathrm{EBE} = EP_\mathrm{EB}P_\mathrm{BE} + EP_\mathrm{EB^*}P_\mathrm{B^*E} \quad (48)$$

$$\mathrm{BBE} = BP_\mathrm{BB}P_\mathrm{BE} + EP_\mathrm{EB^*}P_\mathrm{B^*B^*} \quad (49)$$

$$\mathrm{EBB} = EP_\mathrm{EB}P_\mathrm{BB} + B^*P_\mathrm{B^*B^*}P_\mathrm{B^*E} \quad (50)$$

$$\mathrm{BEB} = BP_\mathrm{BE}P_\mathrm{EB} + B^*P_\mathrm{B^*E}P_\mathrm{EB^*} \quad (51)$$

$$\mathrm{BEB^*} = BP_\mathrm{BE}P_\mathrm{EB^*} \quad (52)$$

$$\mathrm{B^*EB} = B^*P_\mathrm{B^*E}P_\mathrm{EB} \quad (53)$$

$$\mathrm{EBB^*} = EP_\mathrm{EB}P_\mathrm{BB^*} + BP_\mathrm{BB^*}P_\mathrm{B^*E} \quad (54)$$

where P_EE, P_EB, $P_\mathrm{EB^*}$, P_BE, P_BB, $P_\mathrm{BB^*}$, $P_\mathrm{B^*E}$, $P_\mathrm{B^*B}$, and $P_\mathrm{B^*B^*}$ are conditional probabilities. These equations are based on the assumption that copolymer is produced at only one type of active site.

At first, we can calculate the triad distributions [BEB*], [B*EB], and [EBB*] if the polymerization is presumed to follow the first-order Markovian process as

$$[\mathrm{EBB^*}] + 2[\mathrm{B^*EB}] = T_\mathrm{A}/TTA \quad (55)$$

$$2[\mathrm{BEB^*}] + 2[\mathrm{B^*EEB}] = 2[\mathrm{BEB^*}] + 2P_\mathrm{EE}[\mathrm{B^*EB}] = T_\mathrm{F}/TTA \quad (56)$$

$$[\mathrm{EBB^*}] = 2([\mathrm{B^*EB}] - [\mathrm{BEB^*}])/(1 - P_\mathrm{EE}) \quad (57)$$

where P_EE = [EE]/[E]. Equation 57 can be derived as follows:

$$[\mathrm{BB^*}] = ([\mathrm{B^*EB}] - [\mathrm{BEB^*}])/(1 - P_\mathrm{EE}) \quad (58)$$

This equation was derived by Smith.[6]

In our case

$$\begin{aligned}\mathrm{BB^*} &= \overrightarrow{\mathrm{EBB^*}} + \overrightarrow{\mathrm{BBB^*}} + \overrightarrow{\mathrm{B^*BB^*}} = \overrightarrow{\mathrm{EBB^*}} \\ &= \overrightarrow{\mathrm{BB^*E}} + \overrightarrow{\mathrm{BB^*B}} + \overrightarrow{\mathrm{BB^*B^*}} = \overrightarrow{\mathrm{BB^*E}}\end{aligned}$$

or

$$2[\mathrm{BB^*}] = \overrightarrow{\mathrm{EBB^*}} + \overrightarrow{\mathrm{BB^*E}} = [\mathrm{EBB^*}] \quad (59)$$

From eqs 58 and 59, eq 57 can be derived. The calculated values are listed in Table II.

Next, we have to calculate the conditional probabilities and comonomer contents. It is possible to calculate these values on the basis of the following equations:

$$P_{EE} + P_{EB} + P_{EB^*} = 1 \tag{60}$$

$$P_{BE} + P_{BB} + P_{BB^*} = 1 \tag{61}$$

$$P_{B^*E} + P_{B^*B^*} = 1 \tag{62}$$

$$E + B + B^* = 1 \tag{63}$$

$$BP_{BE} + B^*P_{B^*E} = [EB]/2 \tag{64}$$

$$B = EP_{EB} \qquad (BB^* = \overrightarrow{EBB^*}) \tag{65}$$

$$P_{B^*E} = 1 \qquad (BB^* = \overrightarrow{BB^*E}) \tag{66}$$

$$BP_{BE}P_{EB^*} = [BEB^*] \tag{67}$$

$$B^*P_{B^*E}P_{EB} = [B^*EB] \tag{68}$$

The probability P_{B^*B} is taken to be zero, since B*B is not found in the spectrum. The results are listed in Table III.

On the basis of the conditional probabilities, comonomer contents, and eqs 45–54, the triad distributions were calculated. It is clear that the observed values agree well with the calculated ones (see Table II), and it should be confirmed that the polymerization follows the first-order Markovian process, or the terminal model.

Included in Table II for comparison are the calculated triad distributions according to a Bernoullian process which corresponds to statistically random copolymerization. Each triad distribution is calculated on the basis of the following equations, respectively:

$$\mathrm{EEE} = E^3 \tag{69}$$

$$\mathrm{BEE} = BE^2 + E^2B^* = E^2(B + B^*) \tag{70}$$

$$\mathrm{EEB} = E^2B + B^*E^2 = E^2(B + B^*) \tag{71}$$

$$\mathrm{EBE} = EBE + EB^*E = E^2(B + B^*) \tag{72}$$

$$\mathrm{BBE} = B^2E + EB^{*2} = E(B^2 + B^{*2}) \tag{73}$$

$$\mathrm{EBB} = EB^2 + B^{*2}E = E(B^2 + B^{*2}) \tag{74}$$

$$\mathrm{BEB} = BEB + B^*EB^* = E(B^2 + B^{*2}) \tag{75}$$

$$\mathrm{BEB^*} = BEB^* = EBB^* \tag{76}$$

$$\mathrm{B^*EB} = B^*EB = EBB^* \tag{77}$$

$$\mathrm{EBB^*} = EBB^* + BB^*E = 2EBB^* \tag{78}$$

$$\mathrm{EB^*B} = EB^*B + B^*BE = 2EBB^* \tag{79}$$

$$\mathrm{BBB} = BBB + B^*B^*B^* = B^3 + B^{*3} \tag{80}$$

EEE, BEE, EEB, and EBE can be calculated without assumption; however, other triad distributions require using one of them. We chose BEB for this purpose. It is clear that the triad distribution observed is not well represented by a Bernoullian process.

Branching Distribution. It was assumed that copolymer was produced at only one type of active site in a soluble vanadium-based catalytic system $VOCl_3/Al_2(C_2H_5)_3Cl_3$ on calculation of the triad distributions. Using the conditional probabilities and comonomer mole fractions, we can confirm this assumption. If the catalyst has only one type of active site, the branching distribution of the copolymer was calculated theoretically

$$W(y) = {}^3/_4\left(1 - \frac{y}{1+B}\right)\left(\frac{\lambda}{2EBK}\right)^{1/2}\frac{1}{\left(1 + \dfrac{\lambda y^2}{2EBK}\right)^{5/2}}$$

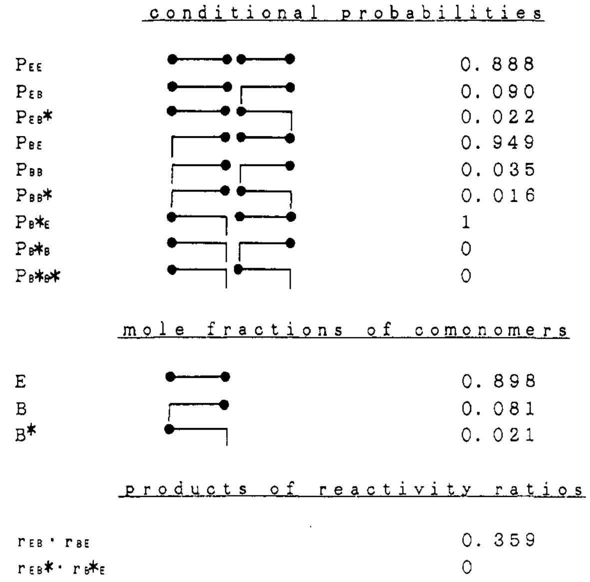
$$K = (1 + 4(r_1r_2 - 1)EB)^{1/2} \tag{81}$$

where $W(y)$ is the weight fraction of the polymer chains, λ is the number-average length, y is the compositional deviation from the average mole fraction of 1-butene, E and B are the average mole fractions of ethylene and 1-butene, respectively, and r_1r_2 is the product of the reactivity ratio.[1,12] r_1r_2 is calculated without taking into account the mode of the 1-butene insertion. In the case of the existence of the secondary insertion, r_1r_2 becomes the average value of primary and secondary insertions.

To elucidate whether the examined copolymer was produced with only one type of active site or with multiple active sites, we shall compare the branching distribution of the copolymer determined by TREF with that of the copolymer model based on eq 81. The value of each parameter of eq 81 is $E = 0.898$, $B = 0.102$, $\lambda = 1170$, and $r_1r_2 = 0.34$ (Appendix). The branching distributions of the copolymer determined by TREF and that of the copolymer model are shown in Figure 2. It is clear that the branching distribution of copolymer determined by TREF agrees well with that of the copolymer model. That is, we can assume that a soluble vanadium-based catalyst has only one type of active site.

In the case of the branching distribution of copolymer prepared with a heterogeneous SiO_2-supported catalytic system $TiCl_4/Al(C_2H_5)_3$, a similar comparison is shown in Figure 3. The value of each parameter of eq 81 is $E = 0.905$, $B = 0.095$, $\lambda = 923$, and $r_1r_2 = 0.97$. In this case, it is clear that the branching distribution of copolymer determined by TREF is much broader than that of the copolymer model, which is obtained by only one type of active site. We can assume that a heterogeneous titanium-based catalyst has multiple active sites. Therefore, it is obvious that a soluble vanadium-based catalyst produces a copolymer with very narrow branching distribution and

Table III
Conditional Probabilities P, Mole Fractions of Comonomers Ethylene (E) and 1-Butene (B, B^*), and Products of Reactivity Ratios $r_{EB}r_{BE}$ and $r_{EB^*}r_{B^*E}$ for Copolymer



conditional probabilities	
P_{EE}	0.888
P_{EB}	0.090
P_{EB^*}	0.022
P_{BE}	0.949
P_{BB}	0.035
P_{BB^*}	0.016
P_{B^*E}	1
P_{B^*B}	0
$P_{B^*B^*}$	0
mole fractions of comonomers	
E	0.898
B	0.081
B*	0.021
products of reactivity ratios	
$r_{EB} \cdot r_{BE}$	0.359
$r_{EB^*} \cdot r_{B^*E}$	0

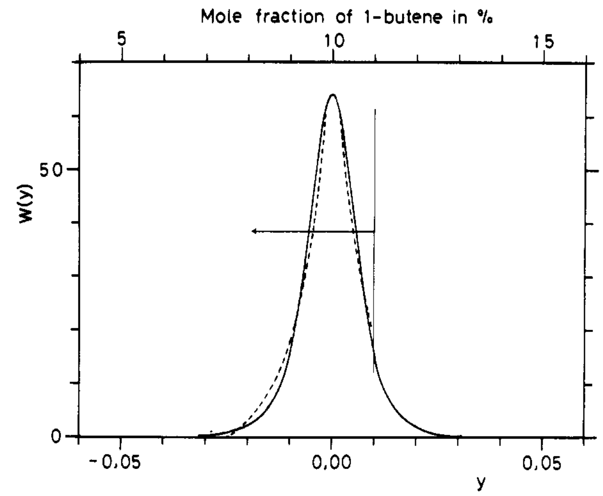


Figure 2. Branching distribution of ethylene/1-butene copolymer in the case of a soluble vanadium-based catalytic system $VOCl_3/Al_2(C_2H_5)_3Cl_3$: (—) branching distribution of copolymer model; (- - -) branching distribution determined by TREF.

a heterogeneous titanium-based catalyst produces a copolymer with very broad branching distribution.

The branching distribution determined by TREF is shown in the case that the mole fraction of 1-butene in copolymer is lower than 11 mol %. This is because our instrument does not have a cooling system and cannot analyze the branching distribution of the copolymer fraction which dissolves in ODCB at room temperature.

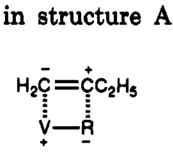
Consideration of Active Sites. Table III shows that a soluble vanadium-based catalytic system $VOCl_3/Al_2(C_2H_5)_3Cl_3$ produces a copolymer having an alternating-type sequence distribution because $r_{EB}r_{BE}$ (=0.36) is much smaller than unity and $r_{EB*}r_{B*E}$ is zero. $r_{EB}r_{BE}$ and $r_{EB*}r_{B*E}$ are defined as follows:

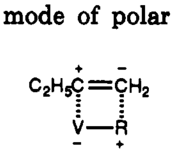
$$r_{EB}r_{BE} = \frac{P_{EE}P_{BB}}{P_{EB}P_{BE}} \qquad r_{EB*}r_{B*E} = \frac{P_{EE}P_{B*B*}}{P_{EB*}P_{B*E}} \tag{82}$$

This copolymer has an irregular linkage of 1-butene units, i.e., a tail-to-tail arrangement and 80% of 1-butene units in copolymer follow the primary insertion. An irregular linkage of 1-butene units corresponding to a head-to-head arrangement could not be observed. Incorporation of 1-butene into growing chains ending with an ethylene or primary 1-butene unit is mostly primary. However, there is no incorporation of 1-butene into growing chains ending with a secondary 1-butene unit. We can assume that an alternating-type sequence distribution comes from the difficulty of 1-butene insertion into growing chains ending with a secondary 1-butene unit. These results tell us that primary addition is dominant if the steric repulsion between the last unit of growing chain and the ethyl group of complexed 1-butene is not effective. Such regioselectivity could mean that the polarization of the V–R bond is shown in structure A. This mode of polarization is opposite to that of the polarization proposed by Boor as shown in structure B.[13] If the polarization of the V–R bond were shown as structure B, incorporation of 1-butene into the growing chains ending with an ethylene or primary 1-butene unit would be mostly secondary. However, this assumption is not consistent with our study. The results mentioned above may come from the steric repulsions between the chlorine ligands on the vanadium atom and ethyl group of complexed 1-butene.


tail-to-tail arrangement


head-to-head arrangement


A


B

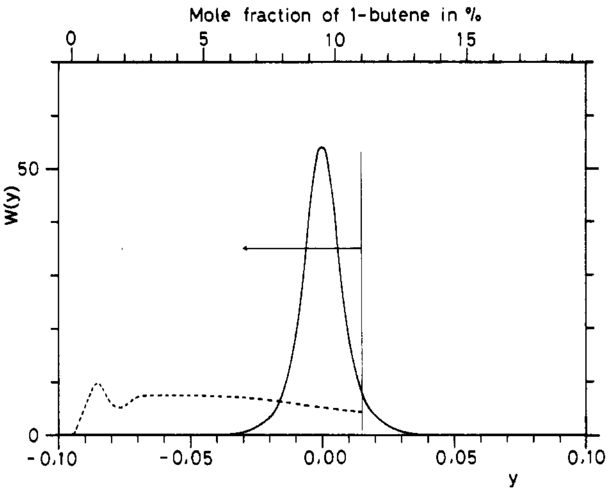
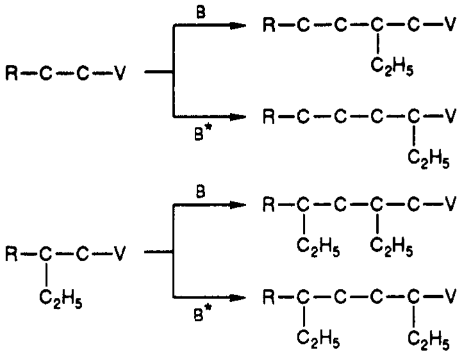


Figure 3. Branching distribution of ethylene/1-butene copolymer in the case of a heterogeneous titanium-based SiO_2-supported catalytic system $TiCl_4/Al(C_2H_5)_3$: (—) branching distribution of copolymer model; (- - -) branching distribution determined by TREF.

In the case of soluble vanadium-based catalysts, secondary insertion is generally believed to occur in the propagation reaction.[14] However, Zambelli et al. suggested that the situation seems to be more complicated.[15] They investigated the ethylene/propylene copolymers obtained with a soluble $VCl_4/Al(C_2H_5)_2Cl$ catalyst and concluded that the insertion of propylene follows a first-order Markovian process; i.e., incorporation of propylene into growing chains ending with a secondary propylene unit is mostly secondary, while incorporation into growing chains with an ethylene or a primary propylene is mostly primary. In this case, however, there is no precise determination of conditional probabilities or propagation rate constants which represent the copolymerization mechanism, and their conclusion is greatly dependent on the ^{13}C NMR analysis of the initiation step. In practice, there is no clear evidence that the initiation and propagation reactions follow the same reaction mechanism. Our detailed analysis indicates clearly that incorporation into growing chains with an ethylene or a primary 1-butene is mostly primary, although this has been indicated by Zambelli et al. in the case of ethylene/propylene copolymer. Moreover, our analysis also confirms no existence of 1-butene units incorporated into growing chains ending with a secondary 1-butene unit. We attribute this difference to the bulkiness between CH_3 and C_2H_5.

On the basis of the conditional probabilities shown in Table III, we can discuss in more detail the propagation reaction mechanism. When it is confirmed that the reaction mechanism follows a first-order Markovian process, each step of 1-butene insertion can be shown as follows:



Here, we do not consider the step of 1-butene insertion to the R–CC(C_2H_5)V bond since P_{B^*B} and $P_{B^*B^*}$ are zero.

The differences between activation energy of primary and secondary insertions of 1-butene into the growing chains ending with ethylene or 1-butene units can be calculated as follows, respectively.

$$\frac{P_{EB}}{P_{EB^*}} = \frac{k_{EB}}{k_{EB^*}} = \exp\left(\frac{G_{EB^*} - G_{EB}}{RT}\right) \qquad (83)$$

$$\frac{P_{BB}}{P_{BB^*}} = \frac{k_{BB}}{k_{BB^*}} = \exp\left(\frac{G_{BB^*} - G_{BB}}{RT}\right) \qquad (84)$$

Here, k_{EB}, k_{EB^*}, k_{BB}, and k_{BB^*} are propagation rate constants and G_{EB}, G_{EB^*}, G_{BB}, and G_{BB^*} are the activation energies of each step. These equations were derived on the basis of the assumption that the preexponential factors of the kinetic rate constants are proportional to the modes of insertion.[16]

From the values of conditional probabilities, we can evaluate as follows.

$$\Delta G_1 = G_{EB^*} - G_{EB} = 0.82 \text{ kcal/mol} \qquad (85)$$

$$\Delta G_2 = G_{BB^*} - G_{BB} = 0.46 \text{ kcal/mol} \qquad (86)$$

On the basis of the assumption that the polarizability of the E–V bond is mostly the same as that of B–V bond, this difference between ΔG_1 and ΔG_2 seems to come from the steric repulsion between the ethyl group of the last unit of the growing chain and that of complexed 1-butene because $G_{BB^*} \geq G_{EB^*}$ and $G_{BB} > G_{EB}$ as shown in Figure 4. Proposed models of active sites on a soluble vanadium-based catalytic system must explain these results.[17]

In the case of ethylene/1-butene copolymerization using the heterogeneous titanium-based catalyst such as SiO_2-supported $TiCl_4/Al(C_2H_5)_3$, there is no existence of the irregular linkages of 1-butene units in the copolymer chain, and it is considered that the propagation step follows the primary insertion. The difference between a soluble vanadium-based and a heterogeneous titanium-based catalyst is attributable to the existence of secondary insertion of 1-butene. We consider the steric repulsion between chlorine ligands on the titanium atom and the ethyl group of complexed 1-butene more effective than the corresponding steric repulsion in a soluble vanadium-based catalyst. We can assume that the vanadium atom ligand is loosely packed compared to that of the titanium atom. Coordination number of vanadium might be less than that of titanium.[18]

Heterogeneous titanium-based catalyst produces an ethylene/1-butene copolymer having a random-type sequence distribution, that is, a Bernoullian sequence distribution. These results tell us that the relationships $k_{EE} \approx k_{BE}$ and $k_{EB} \approx k_{BB}$, namely, $G_{EE} \approx G_{BE}$ and $G_{EB} \approx G_{BB}$, can be expected to hold. In this case, there is no steric repulsion between the ethyl group of the last unit of the growing chain and that of complexed 1-butene in the case of primary insertion. This result is different from that of a soluble vanadium-based catalyst. We conclude that this difference results from the differences of the packed states of ligands of titanium and vanadium atoms as mentioned above.

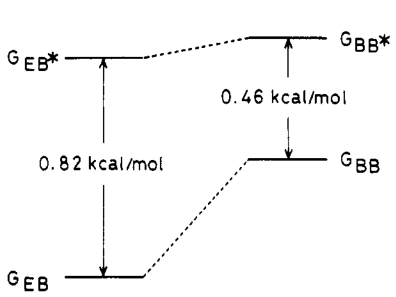


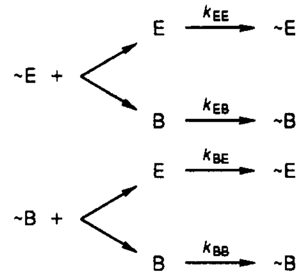
Figure 4. Relationship between each activation energy, G_{EB}, G_{EB^*}, G_{BB}, and G_{BB^*}.

In closing, we feel these analytical methods can be used to obtain insight into the nature of active sites of other catalytic systems.

Acknowledgment. We gratefully acknowledge the critical comments and stimulating suggestions of Prof. T. Tsuruta (Science University of Tokyo). We are indebted to Nippon Oil Co. Ltd. for permission to publish these results.

Appendix

Derivation of r_1r_2 for Copolymer Prepared with a Soluble Vanadium-Based Catalyst. Equation 81 was derived by assuming the following reaction schemes (terminal model) without taking into account the mode of 1-butene insertion

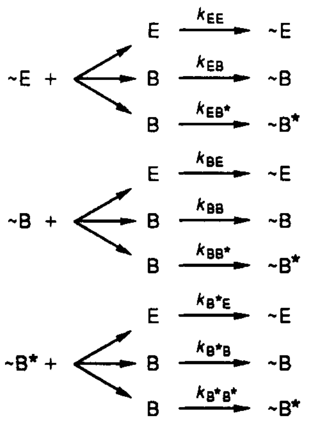


where ~E and ~B are active sites corresponding to –E–(metal) and –B–(metal); k_{EE}, k_{EB}, k_{BE}, and k_{BB} are the propagation rate constants of each step. In this case, the Mayo–Lewis equation takes a well-known form

$$\frac{d[E]}{d[B]} = \frac{[E]}{[B]}\frac{r_1[E] + [B]}{r_2[B] + [E]} \qquad (A1)$$

where $r_1 = k_{EE}/k_{EB}$ and $r_2 = k_{BB}/k_{BE}$, d[E] and d[B] are the mole fractions of ethylene and 1-butene in the copolymer, and [E] and [B] are those in the reaction medium. If there are primary and secondary insertions, r_1r_2 becomes the average value of those of primary and secondary insertions.

When we consider the mode of 1-butene insertion, there will be nine elementary growth reactions. These reactions and their corresponding propagation rate constants can be written as follows:



The rates of monomer consumption are then given by

$$-\frac{\mathrm{d}[\mathrm{E}]}{\mathrm{d}t} = k_{\mathrm{EE}}[\sim\mathrm{E}][\mathrm{E}] + k_{\mathrm{BE}}[\sim\mathrm{B}][\mathrm{E}] + k_{\mathrm{B*E}}[\sim\mathrm{B^*}][\mathrm{E}] \tag{A2}$$

$$-\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_{\mathrm{EB}}[\sim\mathrm{E}][\mathrm{B}] + k_{\mathrm{EB*}}[\sim\mathrm{E}][\mathrm{B}] + k_{\mathrm{BB}}[\sim\mathrm{B}][\mathrm{B}] + k_{\mathrm{BB*}}[\sim\mathrm{B}][\mathrm{B}] \tag{A3}$$

where $[\sim\mathrm{E}]$, $[\sim\mathrm{B}]$, and $[\sim\mathrm{B^*}]$ are the concentrations of the active sites. Here, we can assume that $k_{\mathrm{B*B}}[\sim\mathrm{B^*}][\mathrm{B}] + k_{\mathrm{B*B*}}[\sim\mathrm{B^*}][\mathrm{B}]$ is negligible compared to the other terms of eq A3 since $P_{\mathrm{B*B}}$ and $P_{\mathrm{B*B*}}$ are nearly zero.

Dividing eq A2 by eq A3 yields

$$\frac{\mathrm{d}[\mathrm{E}]}{\mathrm{d}[\mathrm{B}]} = \frac{k_{\mathrm{EE}}[\sim\mathrm{E}][\mathrm{E}] + k_{\mathrm{BE}}[\sim\mathrm{B}][\mathrm{E}] + k_{\mathrm{B*E}}[\sim\mathrm{B^*}][\mathrm{E}]}{k_{\mathrm{EB}}[\sim\mathrm{E}][\mathrm{B}] + k_{\mathrm{EB*}}[\sim\mathrm{E}][\mathrm{B}] + k_{\mathrm{BB}}[\sim\mathrm{B}][\mathrm{B}] + k_{\mathrm{BB*}}[\sim\mathrm{B}][\mathrm{B}]} \tag{A4}$$

If we assume the steady-state conditions, the following equations can be obtained:

$$\begin{aligned} k_{\mathrm{EB}}[\sim\mathrm{E}][\mathrm{B}] + k_{\mathrm{EB*}}[\sim\mathrm{E}][\mathrm{B}] &= k_{\mathrm{BE}}[\sim\mathrm{B}][\mathrm{E}] + k_{\mathrm{B*E}}[\sim\mathrm{B^*}][\mathrm{E}] \\ k_{\mathrm{BE}}[\sim\mathrm{B}][\mathrm{E}] + k_{\mathrm{BB*}}[\sim\mathrm{B}][\mathrm{B}] &= k_{\mathrm{EB}}[\sim\mathrm{E}][\mathrm{B}] \\ k_{\mathrm{B*E}}[\sim\mathrm{B^*}][\mathrm{E}] &= k_{\mathrm{EB*}}[\sim\mathrm{E}][\mathrm{B}] + k_{\mathrm{BB*}}[\sim\mathrm{B}][\mathrm{B}] \end{aligned} \tag{A5}$$

Using eq A5, we can eliminate $[\sim\mathrm{E}]$ and $[\sim\mathrm{B}]$ contained in eq A4. The results are

$$\begin{aligned} \frac{\mathrm{d}[\mathrm{E}]}{\mathrm{d}[\mathrm{B}]} &= \frac{(k_{\mathrm{BE}}[\mathrm{E}] + k_{\mathrm{BB*}}[\mathrm{B}])\{k_{\mathrm{EE}}[\mathrm{E}] + (k_{\mathrm{EB}} + k_{\mathrm{EB*}})[\mathrm{B}]\}}{(k_{\mathrm{EB}} + k_{\mathrm{EB*}})(k_{\mathrm{BE}}[\mathrm{E}] + k_{\mathrm{BB*}}[\mathrm{B}])[\mathrm{B}] + k_{\mathrm{EB}}(k_{\mathrm{BB}} + k_{\mathrm{BB*}})[\mathrm{B}]^2} \\ &= \frac{[\mathrm{E}]}{[\mathrm{B}]} \frac{\dfrac{k_{\mathrm{EE}}}{k_{\mathrm{EB}} + k_{\mathrm{EB*}}}[\mathrm{E}] + [\mathrm{B}]}{\dfrac{k_{\mathrm{EB}}(k_{\mathrm{BB}} + k_{\mathrm{BB*}})}{k_{\mathrm{BE}}(k_{\mathrm{EB}} + k_{\mathrm{EB*}})}[\mathrm{B}] + [\mathrm{E}]} \end{aligned} \tag{A6}$$

where $k_{\mathrm{BB*}}[\mathrm{B}]$ is negligible compared to $k_{\mathrm{BE}}[\mathrm{E}]$.

Comparison of eqs A1 and A6 shows that

$$r_1 = \frac{k_{\mathrm{EE}}}{k_{\mathrm{EB}} + k_{\mathrm{EB*}}} \qquad r_2 = \frac{k_{\mathrm{EB}}(k_{\mathrm{BB}} + k_{\mathrm{BB*}})}{k_{\mathrm{BE}}(k_{\mathrm{EB}} + k_{\mathrm{EB*}})} \tag{A7}$$

That is, we can use eq A7 to calculate the r_1r_2 of eq 81 in the case of a soluble vanadium-based catalyst. Using the conditional probabilities, r_1r_2 leads to the next equation:

$$\begin{aligned} r_1r_2 &= \frac{k_{\mathrm{EE}}k_{\mathrm{EB}}(k_{\mathrm{BB}} + k_{\mathrm{BB*}})}{k_{\mathrm{BE}}(k_{\mathrm{EB}} + k_{\mathrm{EB*}})^2} \\ &= \frac{P_{\mathrm{EE}}P_{\mathrm{EB}}(P_{\mathrm{BB}} + P_{\mathrm{BB*}})}{P_{\mathrm{BE}}(P_{\mathrm{EB}} + P_{\mathrm{EB*}})^2} \end{aligned} \tag{A8}$$

r_1r_2 calculated from eq A8 is 0.34.

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Registry No. $VOCl_3$, 7727-18-6; $Al_2(C_2H_5)_3Cl_3$, 12075-68-2; $TiCl_4$, 7550-45-0; SiO_2, 7631-86-9; $Al(C_2H_5)_3$, 97-93-8; ethylene/1-butene (copolymer), 25087-34-7; ethylene, 74-85-1; 1-butene, 106-98-9.