Studies on the Mechanism of Butadiene–Propene Alternating Copolymerization Using the $\text{VO}[\text{OCH}_2\text{C}(\text{CH}_3)_3]_2\text{Cl}-\text{Al}i\text{Bu}_3$ Catalyst

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ABSTRACT: The average valence of the vanadium ion in $\text{VO}[\text{OCH}_2\text{C}(\text{CH}_3)_3]_2\text{Cl}-\text{Al}i\text{Bu}_3$ reaction product was measured by a potentiometric method. The number of active centers at -30 – -80°C was measured by kinetic extrapolation. The active center was assumed to be mainly V^{+3} . By analysis of the IR spectrum of reaction product of two catalyst components, the $\text{Al}-\text{O}-\text{V}$, $\text{Al}-\text{O}$, and $\text{V}-\text{Cl}$ bonds were confirmed. Probably the active center was V^{+3} having a regular octahedral structure with $\text{Al}-\text{Cl}-\text{V}$ and $\text{Al}-\text{O}-\text{V}$ bridge bonds. Electron donation from butadiene to V^{+3} makes possible a complex formation between them and chain initiation. The propagation is considered to be controlled by coordinating site, a transfer to the monomer was found to be the dominating factor for termination reaction at -30 to -60°C .

KEY WORDS Alternating Copolymerization / Average Valence of V / Mechanism / Structure of Active Center / Initiation / Propagation / Termination /

In regard to the mechanism of the butadiene–propene alternating copolymerization on a V catalyst, Furukawa suggested that¹ the relaxed associated V compound with a two valence is the active center which dissociates in the presence of butadiene and starts chain initiation. The propagation is controlled by coordinating number and the chain terminates through a β -H transfer of the propene end. Our catalytic system differs from that of Furukawa's in the following respects: high polymerization activity, an alternating copolymer with high molecular weight can be obtained ($[\eta] = 2.6 \text{ dl g}^{-1}$); there is no need to age the catalyst components, after aging, the activity lowered,² and the V has had two ligands $-\text{OCH}_2\text{C}(\text{CH}_3)_3$ difficult to reduce by $\text{Al}i\text{Bu}_3$. Thus both the active centers and reaction mechanisms of the systems differ. In order to determine the structure and properties of

the active center, potentiometric titration was carried out to measure the average valence of the vanadium ion formed through the reaction of $\text{VO}[\text{OCH}_2\text{C}(\text{CH}_3)_3]_2\text{Cl}-\text{Al}i\text{Bu}_3$ and the UV-VIS spectrum was used to confirm this measurement. The number of active centers at -30 – 80°C was measured by kinetic extrapolation. The active center was considered to be mainly V^{+3} . By analysis of the IR spectrum of the reaction products of two catalyst components, the $\text{Al}-\text{O}-\text{V}$, $\text{Al}-\text{O}$, and $\text{V}-\text{Cl}$ bonds were confirmed. Thus, it appears that the active center was V^{+3} having a regular octahedral structure with $\text{Al}-\text{Cl}-\text{V}$ and $\text{Al}-\text{O}-\text{V}$ bridge bonds. Butadiene is coordinating to the active center and starts the chain initiation. The propagation is controlled by coordinating site. Transfer to the monomer (propene) was found to be the dominating factor for termination reaction at -30 to -60°C .

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EXPERIMENTAL

The raw materials, their purification, polymerization conditions, IR and NMR measuring methods used in copolymerization were the same as in the former report.² In the potentiometric titration, $\text{Ce}(\text{SO}_4)_2$ was used instead of KMnO_4 as the oxidant for a more accurate measurement. Determination of the number of active centers and the ratio between the β -H and the monomer transfer was made with a dilatometer. Kinetic parameters were measured by a low temperature thermostat and temperature difference was controlled to $<0.1^\circ\text{C}$.

Potentiometric titration: a certain amount of toluene was placed in a 100 ml reactor cleaned with high pure N_2 . The reactor was cooled to the appropriate temperature, specified amounts of $\text{VO}[\text{OCH}_2\text{C}(\text{CH}_3)_3]_2\text{Cl}$ and $\text{Al}i\text{Bu}_3$ solutions were added, shaken to uniformity within a definite time and poured into 15 ml 6 N H_2SO_4 while being protected from hydrolysis by N_2 . Separates layers were obtained after shaking for 10 min. The water layer was transferred to a sealed electrolytic titration cell and titrated with a 0.04 N $\text{Ce}(\text{SO}_4)_2$ solution. ZD-1 type automatic electrolytic titration instrument was used with a saturated calomel electrode as the reference electrode and platinum electrode as the indicating electrode. All titrations were carried out in the presence of highly pure N_2 . Two peaks appeared at about 0 mV and +500 mV on the titration curve (the electric potentials of these peaks were close to that of the reference³ peak). From the consuming amount of $\text{Ce}(\text{SO}_4)_2$ at equivalent point, the relative contents of V^{+2} and V^{+3} can be calculated.

RESULTS AND DISCUSSION

I. The Valence State of V

1. The Effects of Various Al/V Ratios on the Valence State of V.

The concentrations of various ions with

Table I. The effect of Al/V ratio on valence state of V

No.	Al/V	$\text{V}^{+2}/\%$	$\text{V}^{+3}/\%$	$\text{V}^{+4}/\%$
1	1	0	0	100
2	4	0	70.8	29.2
3	8	3.2	96.8	0
4	12	6.2	93.8	0
5	20	15.7	84.3	0
6	50	21.3	78.7	0

Figure 1. Electrolytic titration curve of various Al/V ratio Curve 1—6, Al/V ratio is 1, 4, 8, 12, 20, 50, respectively.

Figure 2. The visible spectrogram of the hydrolyzing products of catalyst at various Al/V ratios. Curve 1—4, the ratio is 1, 4, 12, 20, respectively.

different valence states were measured at various Al/V ratios and listed in Table I. The titration curves appears in Figure 1.

To verify the accuracy of the measured valence states, the same measuring and UV-VIS ultraviolet spectrophotometer (Democratic Germany) procedure were used to determine

the visible spectrograms of the hydrolytic products of catalyst for various Al/V ratios (Figure 2).

In Figure 2, when the Al/V ratio=1, the characteristic peaks of V^{+4} appear: 760 nm and 650 nm; when Al/V ratio=4, the peak at 760 nm weakens and the characteristic peak of V^{+3} at 410 nm is stronger. When Al/V=12 and Al/V=20, the characteristic peaks of V^{+3} at 420 nm and 620 nm appear mainly. Since the content of V^{2+} is small, its characteristic peak at 560 nm can not be seen. The characteristic peak position of these valence states of V are basically consistent with those of ref 4 and 5.

On comparing various Al/V ratios corresponding to change in the content of V^{+3} (Table I) with the relation between Al/V ratio and polymerization conversion (Figure 3) regularity in the change between them becomes apparent.

From Figure 3, Al/V is about 12 where the polymerization conversion is maximum; when the V^{+3} content is highest, the Al/V ratio is about 8. Thus alkylaluminium not only functions to reduce the vanadium compound to a low valence state but exchange the alkyl for Cl. The product may possibly participate in complexing with the active center (see formula 2). Henrici-Olive⁶ found a similar situation when studying the soluble $VO(acac)_2-AlEt_2Cl$ system.

Figure 3. The effect of Al/V ratio on conversion and content of V^{+3} . Polymerization condition: $V/P=9.5 \times 10^{-4}$; $B/P=3$.

2. The Effect of the Period of Aging Time of the Catalyst on the Valence State of V.

When their temperature are the same, the degree of reduction between the two components of the catalyst depends on the reacting time.⁷ The data in Table II demonstrate this situation.

The results obtained by mapping with the data in Table II and a comparison with polymerization regularity are shown in Figure 4.

In Figure 4, after aging of the two com-

Table II. The effect of catalyst aging time on the valence of V^a

No.	Aging time (min)	$V^{2+}/\%$	$V^{+3}/\%$	Average valence state
1*	Not age	0	100	3.0
2	2	6.8	93.2	2.93
3	40	11.0	89.0	2.89
4	120	16.8	83.2	2.83
5	240	25.3	74.7	2.75

^a $V=0.042$ mM; Al/V=12; $T=-45^\circ\text{C}$.

* Catalyst was added to butadiene directly, after shaking the solution for 2 min then subject to hydrolysis and measures.

Figure 4. The relation between aging time of the catalyst, polymer yield and average valence of V. Polymerization condition: $V/P=9.5 \times 10^{-4}$; $B/P=1$; Al/V=12; $T=-45^\circ\text{C}$.

Table III. The effect of temperature on the valence state of V^a

No.	T/°C	V ⁺² /%	V ⁺³ /%	Average valence state
1	-10	23.8	76.2	2.76
2	-25	20.4	79.6	2.79
3	-45	14.0	84.0	2.86
4	-60	6.3	93.7	2.94
5	-76	0	100	3.0

^a V = 0.14 mM; Al/V = 12; reaction time of the catalyst, 15 s.

Table IV. [P*], α , and k_p values at various polymerization temperature^a

T/°C	[P*] $\times 10^4/\text{M l}^{-1}$	α	$k_p/1 \text{ M}^{-1} \cdot \text{min}^{-1}$
-30	0.48	0.040	3250
-40	0.68	0.057	1515
-50	0.80	0.067	503
-60	0.97	0.082	152
-70	1.10	0.092	48.9
-80	1.20	0.101	11.0

^a Polymerization conditions [M] = 1.25 M l⁻¹; B/P = 1; [V] = 1.19 $\times 10^{-3}$ M l⁻¹; Al/V = 15.

Figure 5. I. Relation between the average valence state of V and reaction temperature of the catalyst. II. Relation between conversion and polymerization temperature. Polymerization condition: V/P = 9.5×10^{-4} ; B/P = 3; Al/V = 12.

ponents of the catalyst, there is a considerable decrease in the activity of the catalyst as a result of reducing the V compound to a low valence state.

3. The Effect of Temperature on the Valence State of V and the Concentration of Active Center.

The results from the two components of V act on each other and measuring the valence state of vanadium are shown in Table III.

From a plotting of the average valence state against the reaction temperature (Figure 5), it is apparent that within the temperature range studied, the two curves in Figure 5 are approximately parallel. Thus there is proportional relation between the polymerization activity and average valence state of active center. The higher the average valence state, the larger is the polymerization activity.

Kinetic extrapolation was carried out to measure the concentration of active center at various temperature and according to $\alpha = [\text{P}^*]/[\text{V}]$, $k_p = K/[\text{P}^*]$ and k_p at the corresponding temperatures were calculated (Table IV).

From Table IV, both [P*] and the utilization efficiency α of the catalyst increase with lowering the temperature from -30 to -80°C by a factor of 1.5. This shows that the rise in utilization efficiency of the catalyst is due completely to [P*]. On comparing the data of V⁺³ in Table III with [P*] and α in Table IV, change with temperature decreases. Although there are some differences in their absolute values, and tendency of the regularity of change is quite similar.

According to the above data, in this system, the total amount of V⁺³ is much more than the number of active centers. These centers may be either active or inactive. According to the change regularity about V⁺³, the active center should mainly be the V⁺³ ion.

II. Formation of the Active Center

The reaction between chlorovanadate and triisobutylaluminium and the formation process of the active center has so far not appeared in the literature. Since the active center was found to be V⁺³ and on the basis of the results of Matkovskii,⁸ Keim *et al.*⁹ regarding the reaction between VOCl₃ and AlR₃, the reduction of VO(OR)₂Cl and the alkylating reaction are considered to take place as

Figure 6. The IR spectrogram before and after the reaction of V and Al.

follows:

where R is $-\text{OCH}_2\text{C}(\text{CH}_3)_3$

The V^{+3} ion- $\text{Al}i\text{Bu}_2\text{Cl}$ complex as determined (2) is probably the active center of alternate copolymerization.

From the IR spectrogram (Figure 6) before and after the reaction of $\text{VO(OR)}_2\text{Cl}$ with $\text{Al}i\text{Bu}_3$, it is evident that the reaction product of Al-V has a spectral band at 910–935 cm^{-1} corresponding to the vibration of the Al-O-V bond.⁸

The new spectral band appearing at about 600 cm^{-1} also corresponds to the characteristic peak of the Al-O bond.¹⁰ The characteristic spectral band representing the vibration of the V-Cl bond at 450 cm^{-1} shows no change from before to after the reaction,¹¹ so that the V-Cl band is still present. Some vacant coordinating number is necessary to polymerize the chain,

so that it will propagate alternatively. The 3d orbit of V^{+3} ion has two unpaired electrons. The valence bond theory of coordinating shows that this orbit can bring about d^2sp^3 hybridization to form an octahedral complex with six coordinating numbers.

Based on the above, we conclude the normal octahedral complex of the active center to have the following structure:

III. The Mechanism of Copolymerization

1. The Initiation and Propagation of Alternating Copolymerization.

The initiation and propagation of this copolymerization on active center of V^{+3} is similar to that described by Furukawa *i.e.*, the active center first reacts with butadiene to form a π -allyl complex which initiates the copolymerization (formula 3):

The formed active center with π -allyl end, since only one coordinating point is left, only propene can coordinate to the vacancy (formula 4). Propene inserted into V-Cl bond following formation of the transition state, butadiene then bring about bidentate coordination with the active center. This process is repeated so that the following alternating structure is obtained.

Table V. Homopolymerization of propene and butadiene^a

No.	Monomer	Conversion	Microstructure/%		
		%	<i>trans</i> -1,4	<i>cis</i> -1,4	1,2
1	propene	0	—	—	—
2	propene	0	—	—	—
3	butadiene	0.7	56.3	13.7	30.0

^a Polymerization conditions: V/P(B) = 9.5×10^{-4} ; Al/V = 12; $T = -45^\circ\text{C}$; $t = 5$ h.

Table VI. The change in the valence of the V ion due to the action of butadiene and catalyst^a

No.	Catalyst feeding order	Reaction time	V ⁺²	V ⁺³	V ⁺⁴
			%	%	%
1	P + Al + V	15 s	0	100	0
2	P + Al + V	2 min	6.4	93.6	0
3	Bd + Al + V	15 s	0	61.2	38.8
4	Bd + Al + V	2 min	0	100	0
5	toluene + Al + V	2 min	6.8	93.2	0

^a [V] = 0.042 mM.

According to this scheme neither propene nor butadiene alone can bring about homopolymerization (Table V). Butadiene stabilizes the active center (Table VI).

2. Termination of the Copolymer Chain

In regard to the end group and reaction terminating of the copolymer, Taniguchi¹³⁾ concluded the end group of copolymer to be $\text{CH}_2=\text{C}-$ (β -methylvinyl) on the basis of an

analysis of the NMR spectrogram of the oligomer of low molecular weight.

As to the alternating copolymer of high molecular weight, there is no reference in the literature concerning whether its end group is β -methylvinyl or some end group of butadiene. The reason for this is that, with increasing molecular weight the peak of the end group can not appear in the NMR spectrogram. To solve this problem, and analysis was made using the IR spectrogram. Since the IR absorbing peak at 890 cm^{-1} representing β -methylvinyl is comparatively characteristic peak even in the IR spectrogram of the copolymer of high molecular weight, it can appear although the intensity of the absorbing peak decreases with an increase in molecular weight. We selected representative samples of various $[\eta]$ from 0.16 to 2.11 and list the ratios of their light density D_{890}/D_{970} (Table VII).

In Table VII the peak at 970 cm^{-1} is the characteristic peak of the *trans*-1,4-butadiene unit in the copolymer chain. The content of the *trans*-1,4 butadiene component in the selected samples changes little and the ratio of this unit to that of propene undergoes no significant change (both close to 1:1). Thus, there may be a proportional relation between D_{890} and the number of repeating unit in copolymer. According to the Beer-Lambert law, this relation would be,

$$D_{970} = a_{970} \cdot b \cdot C_{970} \quad \text{or}$$

$$C_{970} = D_{970} / b \cdot a_{970} \quad (5)$$

Table VII. Relation between D_{890}/D_{970} and $[\eta]$ of the copolymer^a

No.	<i>trans</i> -1,4 %	C ₃ %	$[\eta]$ dl g ⁻¹	$D_{890}/D_{970} \times 10^3$	log $[\eta]$	log (D_{890}/D_{970}) $\times 10^3$
1	95.0	49.0	0.16	68.8	-0.80	1.83
2	94.5	48.5	0.30	45.7	-0.52	1.66
3	97.0	48.5	0.45	35.7	-0.35	1.55
4	95.4	49.0	0.74	12.4	-0.13	1.09
5	94.0	47.0	0.89	6.8	-0.05	0.83
6	95.4	49.0	1.06	7.26	0.03	0.86
7	96.0	47.5	1.28	6.4	0.11	0.80
8	95.0	48.0	1.62	5.5	0.20	0.74
9	94.3	47.5	1.82	4.4	0.26	0.64
10	95.2	48.0	2.11	3.5	0.32	0.54

$$D_{890} = a_{890} \cdot b \cdot C_{890} \quad \text{or}$$

$$C_{890} = D_{890} / b \cdot a_{890} \quad (6)$$

where b is the film thickness, a_{970} and a_{890} , the mole light-absorbing coefficients and C_{970} and C_{890} , the concentrations of *trans*-1,4 butadiene and β -methylvinyl (mol l⁻¹) respectively.

Assuming the end groups of the copolymer all to be β -methylvinyl, and according to the number-average molecular weight definition, the following relation is derived.

$$M_n = \frac{C_{970} \cdot M \cdot k}{C_{890}} \quad (7)$$

where M is the molecular weight of the repeating unit and k , the proportional constant.

Substituting (5) and (6) into (7), we obtain,

$$M_n = \frac{D_{970} \cdot M \cdot a_{890}}{D_{890} \cdot a_{970}} \quad (8)$$

make $k' = M \cdot k \cdot a_{890} / a_{970}$. Thus

$$M_n = k' D_{970} / D_{890} \quad \text{or} \quad D_{890} / D_{970} = k' \frac{1}{M_n} \quad (9)$$

Since $[\eta] = K \cdot M_n^\alpha$, substituting formula (9) into above formula gives,

$$[\eta] = K \cdot k'^{\alpha} (D_{890} / D_{970})^{-\alpha}$$

Putting both sides of the equation into logarithmic form gives,

Figure 7.

The relation between log and $\log \left(\frac{D_{890}}{D_{970}} \times 10^3 \right)$.

$$\log [\eta] = \log (k'^{\alpha} \cdot K) - \alpha \log (D_{890} / D_{970})$$

If the initial supposition is true, a linear relation between $\log [\eta]$ and $\log (D_{890} / D_{970})$ should exist.

The mapping result are shown in Figure 7 which shows a fairly good linear relation. The above data was evaluated by a computer, using the least square method. The linear interrelated coefficient r was 0.98 and the slope of the straight line α , 0.77.

The number-average molecular weight of the unfractionated sample was measured by V.P.O. and the osmotic pressure method as $\alpha = 0.67$. Both α are comparatively close. Since

Table VIII. k_{trm} and k_{trH} values at -30 — -60°C^a

No.	T $^\circ\text{C}$	k_{trH} min^{-1}	k_{trm} $\text{lM}^{-1}\text{min}^{-1}$	$\alpha[\text{V}]$ $[\text{M}]_0 \cdot X \times 10^3$	Proportion %	k_{trm} $k_p \times 10^3$	Proportion %	$k_{\text{trH}} \alpha[\text{V}] \cdot t$ $[\text{M}]_0 \cdot X \times 10^3$	Proportion %
1	-30	0.098	12.3	0.0483	1.19	3.77	93.0	0.236	5.82
2	-40	0.044	4.09	0.0792	2.62	2.70	89.3	0.244	8.07
3	-50	0.020	1.06	0.0705	3.05	2.10	90.8	0.141	6.10
4	-60	0.0062	0.236	0.0993	5.78	1.55	90.3	0.0677	3.94

^a Polymerization conditions are same as Figure 8.

the accuracy of the film method in IR quantitative analysis is somewhat poor, complete consistency in the results can not be expected. In Figure 7, a good linear relation from the low to high molecular weight range is evident. Thus the end groups of the alternating copolymer with high molecular weight are nearly all β -methylvinyl.

Furukawa¹⁴ considered transfer of β -H to be the reason for the formation of β -methylvinyl groups. But in experiment, we found that by increasing the proportion of propene in the feed, the molecular weight of the copolymer decreased markedly.² Consequently there is also the probability of a transfer to the propene monomer, specify form β -methylvinyl end groups.¹²

Transfer to monomer (propene):

A kinetic method was used to distinguish these two transfers and relative proportions.

According to a previous report,¹² by plotting $((1/\bar{P}_n) - (\alpha[\text{V}]/[\text{M}]_0 \cdot X))$ against $[\text{V}] \cdot t/$

Figure 8. The relation, $\left(\frac{1}{\bar{P}_n} - \frac{[\text{P}^*]}{[\text{M}]_0 \cdot X}\right) - \left(\frac{[\text{P}^*] \cdot t}{[\text{M}]_0 \cdot X}\right)$.

Polymerization condition: $[\text{V}] = 1.19 \times 10^{-3} \text{ mol l}^{-1}$; $\text{Al/V} = 15$; $\text{B/P} = 1$; $T = -50 \pm 0.1^\circ\text{C}$; $t = 100 \text{ min}$.

$[\text{M}]_0 \cdot X$ or plotting $(1/\bar{P}_n) - ([\text{P}^*]/[\text{M}]_0 \cdot X)$ against $([\text{P}^*] \cdot t/[\text{M}]_0 \cdot X)$ (Figure 8), a straight line was obtained. The slope was k_{trH} and the intercept, k_{trm}/k_p .

The same experiments were carried out at -30 — -60°C and the data obtained appear in Table VIII.

The data in Table VIII show both k_{trm} and k_{trH} to increase with rise in temperature, the k_{trm} values are all bigger than k_{trH} . The effect of k_{trm} on molecular weight of copolymer was to make transfer to monomer about 90% and transfer of β -H, only 10%. In this catalytic system, transfer to monomer (propene) is thus the main means by which the chain is terminated.

From the above and an analysis of the reacting mechanism, the reasons why the po-

lymerization must be carried out at low temperature are as follows: (1) The reducing function of $\text{Al}i\text{Bu}_3$ for the V center ion can be controlled, lessened and delayed, making as many V^{+3} ion as possible; $[\text{P}^*]$ is high and the α value is much larger at low temperature; (2) When the $-\text{OCH}_2\text{C}(\text{CH}_3)_3$ enters the V component as a ligand, its $+I$ may cause the positive charge of V^{+3} to decrease, so that the attractive force between V^{+3} and $\beta\text{-H}$ is weakened. Consequently, the polymer chain continues to propagate. (3) Transfer to the monomer (propene) can be lessened at low temperature to insure the formation of an alternating copolymer with high molecular weight.

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