

THE EFFECT AND FUNCTION OF $\text{Al}(\text{Bu}_2\text{OR})'$ ON BUTADIENE-PROPYLENE ALTERNATING COPOLYMERIZATION CATALYZED BY $\text{VO}(\text{OR})_2\text{Cl}-\text{Al}(\text{Bu}_3)$ SYSTEM*

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ABSTRACT

Four kinds of $\text{Al}(\text{Bu}_2\text{OR})'$ with different R' were synthesized. The effect of $\text{Al}(\text{Bu}_2\text{OR})'/\text{Al}(\text{Bu}_3)$ mole ratio on the conversion, the $[\eta]$ of copolymer and catalytic efficiency were studied. The conversion was increased obviously and the catalytic efficiency was 2.7 times higher than before. The effect of the amount of $\text{Al}(\text{Bu}_2\text{OR})'$ on the valence state of vanadium ion and the change of the valence state of vanadium ion with reaction temperature and time were studied. The VIS and IR spectra of the ternary-component catalyst system were measured. The model of active center including $\text{Al}(\text{Bu}_2\text{OR})'$ was proposed. The function of $\text{Al}(\text{Bu}_2\text{OR})'$ was explained.

INTRODUCTION

There have been a lot of reports^[1-5] about the preparation of butadiene-propylene(Bd-P) alternating copolymer based on $\text{VO}[\text{OCH}_2\text{C}(\text{CH}_3)_3]_2\text{Cl}-\text{Al}(\text{Bu}_3)$ (abbreviated as $\text{V}-\text{Al}_1$) catalyst system and some theoretical study has been published. But so far there was no significant progress in solving the problems of the system, i.e. low polymerization temperature(-45°C — -78°C) and low catalytic efficiency(1400g rubber/g V at maximum).

The kinetic study and the measurement of the valence state of the $\text{V}-\text{Al}_1$ system showed that the key point of raising the polymerization temperature and catalytic activity lies in increasing the content of active V^{+3} center and depressing the over-reduction of vanadium ion(especially $\text{V}^{+3} \rightarrow \text{V}^{+2}$) as much as possible. Adding $\text{Al}(\text{Bu}_2\text{OR})'(\text{Al}_2)$ into above $\text{V}-\text{Al}_1$ system to lower the reductive capability of $\text{Al}(\text{Bu}_3)$ could be an effective way to solve the above mentioned problems. Four $\text{Al}(\text{Bu}_2\text{OR})'$ were first synthesized and then arranged in pairs with $\text{V}-\text{Al}_1$ to catalyze the alternating copolymerization of Bd-P. The effect of Al_2/Al_1 mole ratio on the valence state of vanadium, conversion of Bd-P, catalytic efficiency and the $[\eta]$ of copolymer were studied. The change of the valence state of vanadium ion and catalytic activity with reaction temperature were investigated. The VIS and IR spectra of $\text{V}-\text{Al}_1-\text{Al}_2$ system were recorded. The results showed that with the change of R' in $\text{Al}(\text{Bu}_2\text{OR})'$ the conversion could be increased by 8—13%. Under suitable prescription the conversion obtained at -20°C could be over 80% and the maximum catalytic efficiency could be 2.7 times as high as the result reported before. $\text{Al}(\text{Bu}_2\text{OR})'$ had the function of increasing V^{+3} and it was possible for it to coordinate with the active center to form two kinds of

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V^{+3} active center in $V-Al_1$ system. One of them was nonactive and activated at high temperature so the catalytic system retained high activity at relatively high temperature. The above results have not been found in the literature.

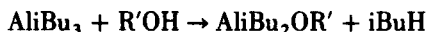
EXPERIMENTAL PART

1. Materials

Phenol(P), isopropyl alcohol(IPA), tertiary butyl alcohol(TBA), tertiary amyl alcohol(TAA), a ll of which were analytically pure, were further dried by $5\text{\AA}$ molecular sieve twice. The purity of the monomers (Bd and P), polymerization procedure and the measurement of the $[\eta]$ of the copolymer were the same as that reported previously^[2].

2. The synthesis of Al_iBu_2OR'

All kinds of Al_iBu_2OR' ($R' = \text{—}\bigcirc\text{—}$, abbreviated as Al_{2P} ; $R' = \text{—CH(CH}_3)_2\text{—}$, abbreviated as Al_{2IP} ; $R' = \text{—C(CH}_3)_3\text{—}$, abbreviated as Al_{2TB} ; $R' = \text{—C(CH}_3)_2CH_2CH_3\text{—}$, abbreviated as Al_{2TA} used in the report were synthesized from Al_iBu_3 and corresponding alcohol through the following reaction:



The reaction was performed in a 100 ml, 3-neck flask which was dried under infrared light and vacuumed and filled with high-pure nitrogen gas alternatively for several times before use. The flask was charged with 50 ml of Al_iBu_3 solution with the concentration of 0.70 mM/ml. The equimolar amount of $R'OH$ in toluene was added dropwise with mechanical stirring. The reaction was stopped when the temperature of the solution dropped to room temperature and the solution was sealed before use.

3. Measurements

The valence state of vanadium ion was measured by redox electric potential titration^[5]. The VIS spectra were recorded on a UV-VIS spectrometer made in East Germany. The IR spectra were recorded on a Shimadzu IR-420 IR spectrometer.

RESULT AND DISCUSSION

1. The catalytic activity of $V-Al_2$ system

It was pointed out by Witte et al.^[6] that when Bd-P alternating copolymerization was catalyzed by $VO(OR)_2Cl-AlR'_3$ system, if the R' in AlR'_3 was a bulky branching isobutyl group, owing to the great space effect between R and R' the catalytic efficiency could reach maximum. If Al_iBu_3 was replaced by $AlEt_2OEt$ the catalytic system showed no activity. The reason was not clear. We considered that the introduction of $-OEt$ group might lower the reduction ability of the Al compound. In order to prove this assumption the Al_iBu_2OR' was paired with $VO[OCH_2C(CH_3)_3]_2Cl$ to catalyze the copolymerization of Bd-P. The result showed that when Al_{2P} , Al_{2IP} , Al_{2TB} and Al_{2TA} were paired with $VO[OCH_2C(CH_3)_3]_2Cl$ respectively to catalyze the copolymerization of Bd-P which was performed in toluene at -45°C all of the formed catalysts did not show any catalytic activity. Because all the R' in Al_iBu_2OR' used were alkyls having some degree of branching the experimental result could be explained as follows: the introduction of OR' caused the lowering or loss of the reduction ability of Al_2 towards V.

2. The effect of Al_2/Al_1 mole ratio

On the premise of constant total materials (calculated on the base of $Al/V = 16$), Al_iBu_2OR'

(Al_2) was used to replace a part of $\text{Al}(\text{iBu})_3$ (Al_1) and the effect of the amount of Al_2 on the alternating copolymerization of Bd-P was assessed by the Al_2/Al_1 mole ratio. The experimental results were summarized in Table 1—3.

Table 1 The effect of $\text{Al}_{2P}/\text{Al}_1$ mole ratio on the conversion and the $[\eta]$ of copolymer

$\text{Al}_{2P}/\text{Al}_1$	Conversion%	$[\eta](\text{dl/g})$
0	68.4	1.56
0.2	74.7	1.48
0.5	80.9	1.51
0.75	74.9	1.46
1.50	62.2	1.42

Polymn. conditions: $\text{Al}/\text{V} = 16$, $\text{V}/\text{P} = 9.5 \times 10^{-4}$, $\text{Bd}/\text{P} = 3$, monomer concentration = 15g/100ml, feeding order: $\text{Bd} + \text{P} + \text{Al}_1 + \text{Al}_2 + \text{V}$, polymn. temp. = -45°C , polymn. time = 5h.

Table 2 The effect of $\text{Al}_{2IP}/\text{Al}_1$ mole ratio on the conversion and the $[\eta]$ of copolymer

$\text{Al}_{2IP}/\text{Al}_1$	Conversion%	$[\eta](\text{dl/g})$
0	68.4	1.56
0.2	75.0	1.56
0.5	77.0	1.58
0.75	74.5	1.57
1.25	69.1	1.53
1.50	64.0	1.51

The polymn. conditions were the same as that in Table 1.

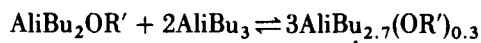
Table 3 The effect of $\text{Al}_{2TA}/\text{Al}_1$ mole ratio on the conversion and the $[\eta]$ of copolymer

$\text{Al}_{2TA}/\text{Al}_1$	Conversion%	$[\eta](\text{dl/g})$
0	68.4	1.56
0.2	81.0	1.41
0.5	81.6	1.43
0.75	79.4	1.38
1.50	66.5	1.36

The polymn. conditions were the same as that in Table 1.

Although the effect of $\text{Al}_{2TB}/\text{Al}_1$ was not presented (for simplification purpose) the same regularity held. It could be seen from these data that both the conversion and the $[\eta]$ of the compolymer could be increased when Al_1 was replaced partially by $\text{Al}(\text{iBu})_2\text{OR}'$. When Al_2/Al_1 equaled 0.5 the conversion and the $[\eta]$ reached maximum and the conversion within experimental range was

increased by 8.6—13.2%. When Al_2/Al_1 was greater than 1 both the conversion and the $[\eta]$ of the copolymer were lower than of previous $V-Al_1$ system. It was considered that Al_2Bu_2OR' had showed the feature of no catalytic activity at this moment. When Al_2/Al_1 equaled 0.5 the following reaction might happen between Al_1 and Al_2 :



Due to the lower reduction capability of $Al_2Bu_{2.7}(OR')_{0.3}$ towards V compound than that of Al_2Bu_3 the over-reduction of V^{+3} to V^{+2} was depressed so the concentration of V^{+3} active center was increased (See Table 6) and the catalytic activity was thus increased.

3. The effect of Al_{2TA} on the catalytic efficiency of $V-Al_1$ system

The previous experimental result showed that among four Al_2Bu_2OR' the activity of Al_{2TA} was the highest. Therefore it was expected that it was possible to further lower the amount of catalyst and increase the catalytic efficiency through the adding of reasonable amount of Al_{2TA} . The experiment results were shown in Table 4.

Table 4 The effect of Al_{2TA} on the catalytic efficiency of $V-Al_1$ system

Amount of catalyst	Conversion	Catalytic efficiency	$[\eta](dl/g)$
$(V/P \times 10^{-4})$	(%)	(g rubber/g V)	
9.5	79.9	1812	1.46
5.6	72.8	2420	1.48
4.5	78.8	3261	1.50
3.4	72.7	4019	1.53

Polymn. conditions: $Al_{2TA}/Al_1 = 0.6$, $Bd/P = 2.3$, monomer conc. = 15.7g/100ml, other conditions the same as that in

Table 1

With the previous $V-Al_1$ system under the same polymerization conditions the highest catalytic efficiency was 1481g rubber/g V and the conversion decreased dramatically when the amount of catalyst was reduced^[2], but in $V-Al_1-Al_{2TA}$ system it was not the case. When the amount of catalyst was reduced, although the conversion was somewhat decreased the catalytic efficiency increased dramatically and could be 2.7 times as that using $V-Al_1$ system. Meanwhile the $[\eta]$ of the copolymer increased to some extent which meant that the $Bd-P$ alternating copolymer with high molecular weight could be produced through the use of $V-Al_1-Al_{2TA}$ system with high activity.

4. The effect of Al_{2TA} on thermostability of $V-Al_1$ system

From the results of kinetic study it was shown that^[4] for the reduction reaction of aluminum, component towards vanadium compound the reduction of the concentration of Al_2Bu_3 was equivalent to the raising of reduction temperature. Therefore, it was expected that the reduction reaction of aluminum component towards vanadium compound could be depressed partially by the adding of Al_{2TA} . To prove this, the effect of Al_{2TA}/Al_1 mole ratio on $Bd-P$ alternating copolymerization catalyzed by $V-Al_1-Al_2$ system was investigated at relatively high temperature (Table 5).

Table 5 The polymerization catalyzed by $\text{V-Al}_1\text{-Al}_2$ system at relatively high temperature

Polymn. temp. (°C)	$\text{Al}_{2\text{TA}}/\text{Al}_1 = 0.2$		$\text{Al}_{2\text{TA}}/\text{Al}_1 = 0.5$		$\text{Al}_{2\text{TA}}/\text{Al}_1 = 0.75$	
	Conversion	$[\eta]$	Conversion	$[\eta]$	Conversion	$[\eta]$
	%	(dl/g)	(%)	(dl/g)	(%)	(dl/g)
-45	81.0	1.41	81.6	1.43	79.4	1.38
-30	67.1	1.16	75.2	1.18	82.8	1.20
-20	67.2	1.02	74.9	1.01	86.8	1.02

Polymn. conditions: $\text{Al}/\text{V} = 16$, $\text{V}/\text{P} = 9.5 \times 10^{-4}$, $\text{Bd}/\text{P} = 3$, monomer conc. = 15g/100ml, feeding order: $\text{Bd} + \text{P} + \text{Al}_1 + \text{Al}_2 + \text{V}$, polymn. time = 5h

The data in Table 5 showed that the conversion depended not only on polymerization temperature but on $\text{Al}_{2\text{TA}}/\text{Al}_1$ mole ratio as well. If the polymerization was carried out at relatively high temperature more $\text{Al}_{2\text{TA}}$ was needed to retain the high activity of the catalytic system. When $\text{Al}_{2\text{TA}}/\text{Al}_1$ equaled 0.75, although the conversion at -20°C was high, the $[\eta]$ of the copolymer was relatively low so certain procedure should be used to depress the decreasing of molecular weight caused by monomer transfer or $\beta\text{-H}$ transfer enhanced at high temperature. It should be pointed out that -45°C and -20°C were two quite different technical and economic index assessing energy consumption. Therefore, the achievement of the above result could be considered as a big progress in V-Al system.

5. The function of $\text{Al}_{2\text{TA}}$ in V-Al_1 system

(1) The effect of $\text{Al}_{2\text{TA}}/\text{Al}_1$ mole ratio on the valence state of vanadium ion (Table 6)

Table 6 The effect of $\text{Al}_{2\text{TA}}/\text{Al}_1$ mole ratio on $\text{V}^{+3}\%$ and average valence state at -45°C

$\text{Al}_{2\text{TA}}/\text{Al}_1$	$\text{V}^{+2} \%$	$\text{V}^{+3} \%$	Average valence state
0	19.0	81.0	2.810
0.2	8.4	91.6	2.916
0.5	6.5	93.5	2.935
0.75	7.0	93.0	2.930
1.25	4.4	95.6	2.956
2.0	2.5	97.5	2.975

Measurement conditions: $\text{Al}/\text{V} = 16$, $[\text{V}] = 0.05 \text{ mM/ml}$, reaction temp. = -45°C , reaction time: 20 min.

The data in Table 6 showed that with the increasing of $\text{Al}_{2\text{TA}}/\text{Al}_1$ mole ratio, both $\text{V}^{+3}\%$ and the average valence state of vanadium ion increased, which illustrated that $\text{Al}_{2\text{TA}}$ was capable to depress the further reduction of V^{+3} to V^{+2} . It had been proved that the active center of V-Al_1 system was regular octahedron complex with V^{+3} as center^[5]. The increasing of $\text{V}^{+3}\%$ should imply the enhance of catalytic activity. To prove this, some contrast experiments of polymerization activity were carried out (Fig. 1).

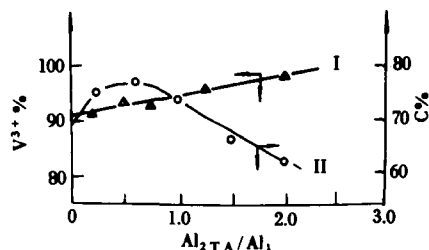


Fig. 1 The effect of $\text{Al}_{2\text{TA}}/\text{Al}_1$ mole ratio on $\text{V}^{3+}\%$ and polymerization conversion

I. Polymn. conditions were the same as that in Table 6

II. Polymn. conditions: $\text{V}/\text{P} = 9.5 \times 10^{-4}$, $\text{Al}/\text{V} = 16$, $\text{Bd}/\text{P} = 3$, $[\text{M}] = 15\text{g}/100\text{ml}$,
polymn. temp.: -45°C , feeding order: $\text{Bd} + \text{P} + \text{Al}_1 + \text{Al}_2 + \text{V}$, polymn. time 5h.

It could be seen by comparing the data of $\text{V}^{3+}\%$ and conversion in Fig. 1 that within the range of $\text{Al}_{2\text{TA}}/\text{Al}_1 = 0 - 0.75$, $\text{V}^{3+}\%$ increased gradually and the conversion grew continuously. These phenomena matched the assumption that the active centre was V^{3+} . But when $\text{Al}_{2\text{TA}}/\text{Al}_1$ stayed in the range of $0.75 - 2.0$, the percentage of V^{3+} grew with $\text{Al}_{2\text{TA}}/\text{Al}_1$ mole ratio increasing, while the conversion decreased gradually. The result was in contradiction with the above assumption. But the data of V^{3+} was obtained 20 minutes after the start of the reaction of $\text{V}-\text{Al}_1-\text{Al}_2$ while the conversion was the final conversion of 5 hrs, it might be suggested that with the proceeding of reaction V^{3+} was over-reduced to V^{2+} , which caused the decreasing of $\text{V}^{3+}\%$. But the experimental data obtained through the extension of reaction denied this possibility (Table 7).

Table 7 The contrast of $\text{V}^{3+}\%$

Reaction time (min.)	$\text{Al}_{2\text{TA}}/\text{Al}_1 = 0.5$			$\text{Al}_{2\text{TA}}/\text{Al}_1 = 1.25$		
	$\text{V}^{2+}\%$	$\text{V}^{3+}\%$	average valence state	$\text{V}^{2+}\%$	$\text{V}^{3+}\%$	average valence state
20	6.5	93.5	2.935	4.4	95.6	2.956
180	32.6	67.4	2.674	5.3	94.7	2.947

The measurement conditions were the same as that in Table 6 except for reaction time.

Table 7 showed that when $\text{Al}_{2\text{TA}}/\text{Al}_1 = 0.5$, $\text{V}^{3+}\%$ decreased dramatically with the extension of reaction time, while $\text{Al}_{2\text{TA}}/\text{Al}_1 = 1.25$, both the percentage of V^{3+} and the average valence state of vanadium ion were basically constant within the same reaction time range, which illustrated that the above mentioned assumption was not in agreement with the experimental result. The second possibility was that because the polymerization temperature was low (-45°C), part of V^{3+} did not show catalytic activity^[5]; when temperature was raised the part of V^{3+} was activated and became the true active center. The rationality of this reasoning would be discussed in the section about the thermostability of the catalyst system.

(2) The stabilizing degree of $\text{Al}_{2\text{TA}}$ towards V^{3+}

In order to investigate the stabilizing degree of $\text{Al}_{2\text{TA}}$ towards V^{3+} , the change of $\text{V}^{3+}\%$ with reaction time was measured at -45°C , with $\text{Al}_{2\text{TA}}/\text{Al}_1 = 0.5$ (Table 8).

Table 8 The change of the concentration of vanadium ion with reaction time

Reaction time(min.)	V ²⁺ %	V ³⁺ %	average valence state
20	6.5	93.5	2.935
60	21.7	78.3	2.783
120	26.1	73.9	2.739
180	32.6	67.4	2.674

Measurement conditions: Al/V = 16, [V] = 0.015 mM/ml, Al₂TA/Al₁ = 0.5, reaction temp.: -45°C.

Compared with the V-Al₁ system without Al₂TA, the decreasing of V³⁺% and average valence state with reaction time was smaller and the changing speed was lower. By comparing the double logarithm lines of V³⁺% - t before and after the adding of Al₂TA it could be found that when the reaction time was shorter than 4 hrs.(Fig.2), V³⁺% in V-Al₁-Al₂TA system was always higher than that in V-Al₁ system, which showed that the adding of Al₂TA could increase the content of V³⁺. In other words Al₂TA had the function of stabilizing V³⁺. The difference in the slopes of two straight lines could be considered as the assessment of the ability of Al₂TA to stabilize V³⁺.

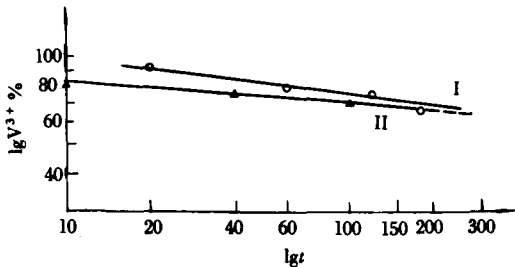


Fig. 2 The change of V³⁺% with reaction time
I. V-Al₁-Al₂TA system
II. V-Al₁ system

(3) The effect of Al₂TA on thermostabilization of V-Al₁ system

One of the expected results of using Al₂TA to partially replace Al₁ was to enable the polymerization to perform at relatively high temperature and to obtain satisfactory catalytic activity

Table 9 The effect of reaction temperature on the valence state of vanadium ion in V-Al₁ system

Reaction temp.(°C)	V ²⁺ %	V ³⁺ %	Average valence state
-45	19.0	81.0	2.810
-25	39.4	60.6	2.606
-10	45.7	54.3	2.543
+10	66.7	33.3	2.333

Measurement conditions: Al/V = 16, [V] = 0.015 mM/ml, reaction time: 20 min.

and $[\eta]$ with the aid of delaying reduction reaction and the stabilizing function of $\text{Al}_{2\text{TA}}$ towards V^{+3} center. In order to prove this expectation the effect of reaction temperature on $\text{V}^{+3}\%$ in $\text{V}-\text{Al}_1$ system with Al_1 being partially replaced by $\text{Al}_{2\text{TA}}$ was investigated (Tables 9 and 10).

Table 10 The effect of reaction temperature on the valence state of vanadium ion in $\text{V}-\text{Al}_1-\text{Al}_{2\text{TA}}$ system

Reaction temp.(°C)	$\text{V}^{+2} \%$	$\text{V}^{+3} \%$	Average valence state
-45	6.5	93.5	2.935
-20	6.7	93.3	2.933
-5	4.2	95.8	2.958
+15	5.1	94.9	2.949

Measurement conditions: $\text{Al}_{2\text{TA}}/\text{Al}_1 = 0.75$, reaction time: 25 min., others were the same as that in Table 9.

By comparing the data in Table 9 and Table 10 it could be seen clearly that before the adding of $\text{Al}_{2\text{TA}}$, when the reaction temperature was raised from -45°C to 10°C , $\text{V}^{+3}\%$ decreased by 47.7% and the average valence state decreased by 0.48; after the addition of $\text{Al}_{2\text{TA}}$ when the reaction temperature was raised from -45°C to 15°C , $\text{V}^{+3}\%$ did not decrease but increased by 1.4%. This phenomenon showed that the $\text{V}-\text{Al}_1-\text{Al}_{2\text{TA}}$ system formed through the partial replacement of Al_1 by $\text{Al}_{2\text{TA}}$ was stable at high temperature.

If the measurement result of valence state and the polymerization result were compared (Fig. 3), it was found that when the reaction temperature was raised from -45°C to -20°C , the average valence state (or $\text{V}^{+3}\%$) of the system was basically the same, but the conversion within this temperature range increased by 8%, which illustrated that the increase of conversion was really caused by the increase of V^{+3} content. If the data of the valence state of vanadium ion ($\text{V}^{+3}\% = 93.3$) and conversion (86.8%) at -20°C in Fig.3 were compared with the data of the valence state of vanadium ion ($\text{V}^{+3}\% = 97.7$) and conversion (67.2%) at -45°C with $\text{Al}_{2\text{TA}}/\text{Al}_1 = 2.0$ in Table 6 and Fig.1, it could be seen that the difference in $\text{V}^{+3}\%$ was very little but the difference in conversion was as high as 20%. The difference was obviously caused by the fact that the "effective" concentration of V^{+3} ion, i.e. the V^{+3} center with initiating function increased at high temperature. In other words, the nonactive V^{+3} at low temperature (-45°C) was partially activated with the temperature increasing and became active center. These data strongly supported the hypothesis that there were two kinds of V^{+3} centers in $\text{V}-\text{Al}_1$ system^[5]. As for the phenomenon in Fig.3 that the $[\eta]$ of the copolymer dropped dramatically with the temperature increasing, it could still be explained by the known regularity that the monomer transfer and the $\beta\text{-H}$ transfer intensified with the temperature increasing.

(4) VIS and IR spectra of $\text{V}-\text{Al}_1-\text{Al}_{2\text{TA}}$ system

The visible light spectra of the hydrolysis product of $\text{V}-\text{Al}_1-\text{Al}_{2\text{TA}}$ were shown in Fig.4.

It could be seen from the absorption peaks in Fig.4 that the positions of the characteristic peaks of V^{+3} ion in $\text{V}-\text{Al}_1$

system (curve II) were 380 nm (λ_{max1}) and 620 nm (λ_{max2}) which were in agreement with the reference^[7]. After the addition of $\text{Al}_{2\text{TA}}$ (no matter added at -45°C or at 15°C) some new peaks appeared at 345 nm and 580nm. It was shown by the result of electric potential titration that there were only V^{+3} and V^{+2} ions present in the system at the moment. Therefore we thought that the

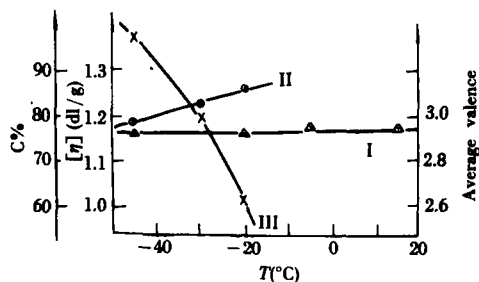


Fig. 3 The effect of temperature on the average valent state of vanadium ion, the conversion and the $[\eta]$ of copolymer
I— average valence. II— conversion III— $[\eta]$ of copolymer

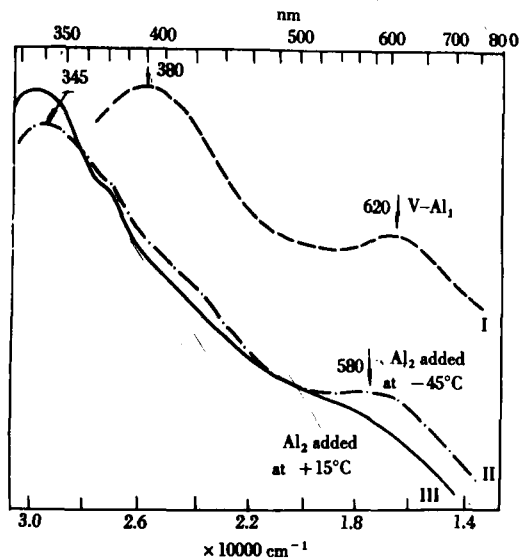


Fig. 4 The visible light spectra of the hydrolysis product of V-Al_1 and $\text{V-Al}_1\text{-Al}_{2\text{TA}}$

Catalyst components and reaction conditions:

I. V-Al_1 system, $\text{Al}/\text{V} = 16$,

reaction temp.: -45°C , reaction time: 20 min.

II. $\text{V-Al}_1\text{-Al}_{2\text{TA}}$ system, $\text{Al}/\text{V} = 16$, $\text{Al}_{2\text{TA}}/\text{Al}_1 = 0.75$,
others were the same as that in I.

III. $\text{Al}_{2\text{TA}}$ was added at 15°C , others were the same as that in II.

peak at 345 nm could be the characterization of the second kind of V^{+3} and the peak at 580 nm was due to the possibility that the existence of the second kind of V^{+3} made the peak originally at 620 nm (λ_{max}) displace.

The IR spectrm of $\text{V-Al}_1\text{-Al}_{2\text{TA}}$ were shown in Fig.5.

By comparing the positions and the intensities of the absorption peaks of two systems (Fig. 5) it was found that the positions and intensities of the absorption peak at $910\text{--}935\text{ cm}^{-1}$ which characters the vibration of Al-O-V bond^[2], at 610 cm^{-1} which characters the vibration of $\text{Al} \rightarrow \text{O}$ bond^[8] and at 450 cm^{-1} which characters the vibration of V-Cl bond^[9] did not change after the addition of $\text{Al}_{2\text{TA}}$, and the obtained copolymer was still strictly alternating copolymer of Bd-P . These facts illustrated that after the addition of $\text{Al}_{2\text{TA}}$ the originally assumed regular octahedron of

V^{+3} active center still held. The intensity of the absorption peak at $910\text{--}935\text{ cm}^{-1}$ increased relatively which might mean the change of electric charge between $V\text{--}O\text{--}Al$ bonds.

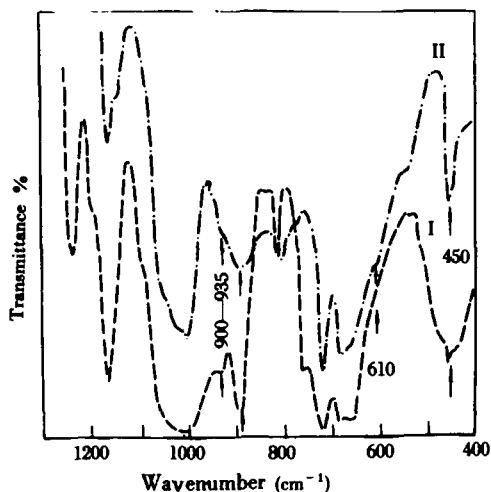
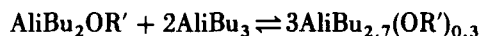


Fig. 5 The IR spectra of the catalytic system before and after Al_I was partially replaced by Al_{2TA}
I. $V\text{--}Al_I$ system II. $V\text{--}Al_I\text{--}Al_{2TA}$ system

6. The reduction reaction in $V\text{--}Al_I\text{--}Al_{2TA}$ system and the model of active center

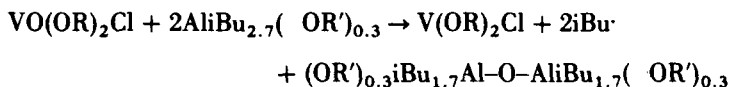
According to above experiment of polymerization activity, the measurement of the valence state and the VIS and IR spectra, we proposed that the reduction reaction in $V\text{--}Al_I\text{--}Al_{2TA}$ system and the process of the formation of the active center were as follows:

(1) The reaction between Al_I and Al_{2TA} may be the exchange equilibrium as below equation:



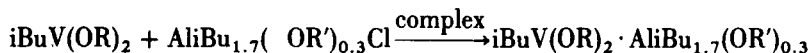
where $R' = -C(CH_3)_2CH_2CH_3$. Because the reduction capability of $AlIBu_{2.7}(OR')_{0.3}$ towards vanadium compound was lower than that of $AlIBu_3$ so the reduction process between $V\text{--}Al$ could be delayed, the over-reduction of V^{+3} to V^{+2} could be depressed, the concentration of V^{+3} center was increased. All of those resulted in the increase of the catalytic activity.

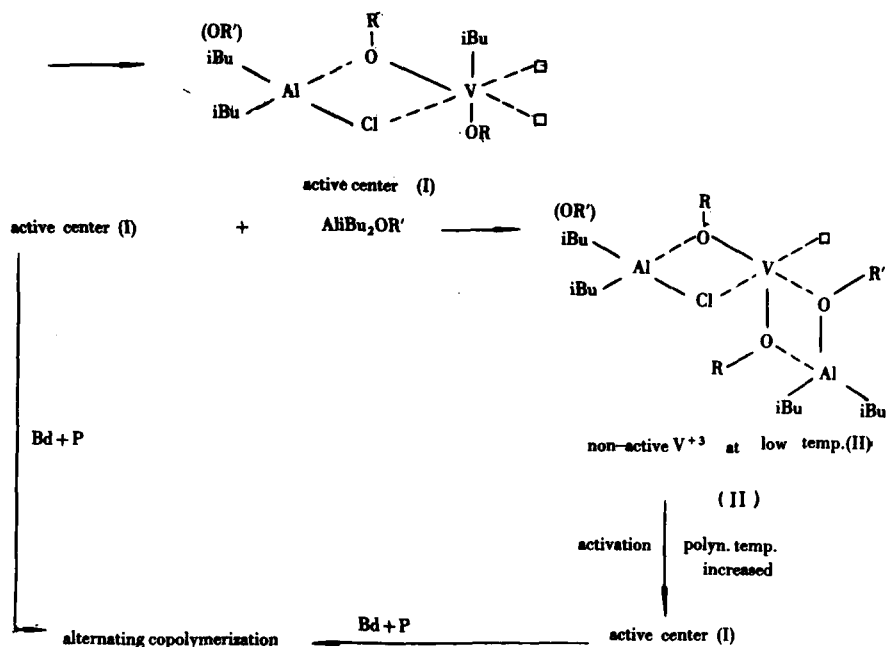
(2) The reduction reaction of $AlIBu_{2.7}(OR')_{0.3}$ towards vanadium compound was as below:



where $R = -CH_2C(CH_3)_3$

(3) The formation and activation of the active center





The data of the polymerization experiments and the measurement of the valence state could be reasonably explained by this model.

Keywords:

Bd-P alternating copolymerization; V-Al catalytic system; Effect of $\text{Al}(\text{iBu})_2\text{OR}'$; V^{3+} active center.

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