

THE EFFECT OF ETHERS ON ALTERNATING COPOLYMERIZATION OF BUTADIENE AND PROPYLENE CATALYZED BY VANADIUM-ALUMINUM SYSTEM*

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ABSTRACT

The effect of five ethers on alternating copolymerization of butadiene and propylene were investigated. It was found that under appropriate conditions, by adding ether into reaction system, the conversion could be increased by 10–20% and the catalytic efficiency doubled at -45°C . The interaction between ether and active center was also studied.

INTRODUCTION

The alternating copolymer of butadiene(Bd) and propylene(P) is a new type of stereoregular rubber whose microstructure and properties are analogous to those of natural rubber and isoprene rubber. Hence, it is important and practical to study the alternating copolymerization of Bd and P for the sake of industrialization of alternating copolymer rubber of Bd-P.

There have been some reports concerning the polymerization conditions, characterization^[1], kinetics^[2], reaction mechanism^[3] of the copolymerization of Bd-P and the model of active center^[4], but the rubber product of alternating copolymer of Bd-P has not yet commercialized due to some shortcomings in this system, such as low polymerization temperature (-45°C — -76°C) and low catalytic efficiency (maximum 1400g rubber/g V). Under such circumstances and based on the study of kinetics and the valence state of active center, an attempt was made by the authors to increase both the polymerization temperature and catalytic efficiency simultaneously by adding ether into vanadium-aluminum catalyst system. It was shown experimentally that among five ethers selected in spite of the amount of ether used to reach the highest catalytic activity varying from one to another, under same experimental conditions the conversion at -45°C could be increased by 10–20% and catalytic efficiency doubled as well. The VIS and IR spectra of hydrolysis product of catalyst system indicated that there was a kind of weak interaction presented between ether and V^{+3} active center.

EXPERIMENTAL

1. Materials

Ethyl ether(ETH), tetrahydrofuran(THF), dioxane(DIO), 1, 2-dimethoxyethane(DME) and diethylene glycol diethyl ether(2G) were analytically pure and further purified and then dried over

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5Å molecular sieve. The purity and grade of monomers(Bd, P) were described previously^[1,2].

2. Procedure and Measurement

The synthesizing procedures of vanadium catalyst and copolymerization of Bd-P, the measurement of the valence state of vanadium ion and the characterization of the obtained copolymer were reported previously^[1,2]. VIS spectra were recorded on a UV-VIS spectrometer made in East Germany and IR spectra on a Shimadzu IR-420 spectrometer made in Japan.

RESULTS AND DISCUSSION

1. The effect of ether on alternating copolymerization of Bd-P

In the early-stage study of alternating copolymerization of Bd and P the research group of Maruzen Petrochemical Company in Japan prepared some catalyst systems that were very stable at relatively high temperature by adding ethanol, acetone, ester, organic carboxylic acid, etc. into $\text{VOCl}_3\text{-AlR}_3$ system^[5]. We selected five ethers, i.e. ETH, THF, DIO, DME and 2G, and investigated their effect on alternating copolymerization of Bd and P catalyzed by $\text{VO}[\text{OCH}_2\text{C}(\text{CH}_3)_3]_3\text{Cl-AliBu}_3$ system and the following results were obtained:

Table 1 The effect of the amount of ether on conversion and $[\eta]$ of copolymer

THF / Al	THF / V	Conversion%	$[\eta]$ (dl / g)
0	0	70.7	1.51
0.025	0.4	76.7	1.49
0.05	0.8	80.9	1.52
0.10	1.6	82.2	1.49
0.15	2.4	77.1	1.49
0.20	3.2	70.3	1.49
0.25	4.0	68.3	1.49
0.35	5.6	66.9	1.51

Polymerization conditions:

$\text{V/P} = 9.5 \times 10^{-4}$, $\text{Al/V} = 16$, $\text{Bd/P} = 3$, $[\text{Bd} + \text{P}] = 15\text{g}/100\text{ml}$, $T = -45^\circ\text{C}$, $t = 4\text{h}$,

feeding order: Bd + P + Al + ether + V

Table 2 The effect of ETH / Al mole ratio on conversion and $[\eta]$ of copolymer

ETH / Al	ETH / V	Conversion%	$[\eta]$ (dl / g)
0	0	71.8	1.50
0.025	0.4	80.6	1.47
0.15	2.4	85.9	1.62
0.20	3.2	85.0	1.60
0.45	7.2	80.9	1.51
0.55	8.8	77.3	1.50
0.65	10.4	75.0	1.48
0.75	12.0	71.9	1.51

Polymerization conditions: the same as that in Table 1

The other ethers DIO, DME and 2G showed similar results. All the experimental data indicated that ethers showed little effect on $[\eta]$ of copolymer formed, and the ether / Al mole ratio through which both the highest catalytic activity and optimum $[\eta]$ could be reached varied with the structure of ether and the number of oxygen atom (Table 3). At optimum mole ratio all five ethers could increase the conversion by 10–19% under the same conditions.

Table 3 The relationship between the structure and properties of ethers and optimum ether / Al mole ratio

Ethers			Optimum ether / Al mole ratio	Conversion (%)	$[\eta]$ (dl / g)
ether	structure	number. of oxygen atom			
THF	cyclic	1	0.1	91.4	1.46
ETH	linear	1	0.015	90.7	1.41
DIO	cyclic	2	0.05	80.3	1.43
DME	linear	2	0.025	93.7	1.44
2G	linear	3	0.02	88.6	1.45

Polymerization conditions: $t = 5h$, others are the same as that in Table 1.

It could be seen from the data in Table 3 that at optimum ether / Al mole ratio the catalytic activity was inversely proportional to the number of oxygen atom. It could be explained by the flexibility of

Table 4 The effect of feeding order on conversion, catalytic efficiency and $[\eta]$ of copolymer

Ether / Al mole ratio	Feeding order	Conversion (%)	Catalytic efficiency (g rubber / g V)	$[\eta]$ (dl / g)
THF / Al = 0.1	Bd + P + Al + THF + V	91.4	1815	1.46
	Bd + P + V + THF + Al	88.9	1764	1.46
	Bd + P + Al + V + THF	83.7	1663	1.45
ETH / Al = 0.15	Bd + P + Al + ETH + V	90.7	1801	1.41
	Bd + P + V + ETH + Al	84.3	1763	1.40
	Bd + P + Al + V + ETH	83.1	1650	1.40
DIO / Al = 0.05	Bd + P + Al + DIO + V	80.3	1593	1.43
	Bd + P + V + DIO + Al	93.4	1855	1.51
	Bd + P + Al + V + DIO	86.3	1715	1.48
DME / Al = 0.025	Bd + P + Al + DME + V	93.7	1861	1.44
	Bd + P + V + DME + Al	95.0	1886	1.45
	Bd + P + Al + V + DME	94.1	1869	1.45
2G / Al = 0.02	Bd + P + Al + 2G + V	88.6	2177	1.39
	Bd + P + V + 2G + Al	81.5	2033	1.42
	Bd + P + Al + V + 2G	70.9	1744	1.35

Polymerization conditions: the same as that in Table 3.

the chain, the coordination of oxygen atom and steric hindrance. The combining influence of electron effect and steric hindrance showed the following sequence: DME $\approx$ 2G > DIO > THF > ETH

The effect of feeding order on conversion, catalytic efficiency and $[\eta]$ of copolymer (Table 4) The data in Table 4 indicated that the feeding order did show some effect on conversion, catalytic efficiency and $[\eta]$ of copolymer but not too much difference from one case to another. The most obvious difference was that among three types of feeding order it was always the last feeding order which gave relatively low conversion and catalytic efficiency for all five ethers. This demonstrated again that in this catalyst system vanadium and aluminum could not be brought together and aged, otherwise the catalytic activity could obviously decrease^[1]. Therefore, the feeding order of Bd + P + Al + ether + V was adopted through the context.

The effect of ethers on catalytic efficiency

Although the conversion under the same polymerization conditions could represent catalytic activity it could not reveal the amount of catalyst used and its effect on polymerization. Therefore it would be better to use the weight of copolymer obtained during specified time through unit vanadium catalyst (g copolymer/g vanadium), i. e. catalytic efficiency as the standard of evaluation. It was worth noticing that when ether was added into the catalyst system the amount of catalyst used could be further decreased and catalytic efficiency increased (Table 5).

Table 5 The effect of ether on catalytic efficiency and $[\eta]$ of copolymer*

Ethers	Conversion (%)	Catalytic efficiency (g rubber / g V)	$[\eta]$ (dl / g)	Catalytic efficiency increase(%)	$\Delta[\eta]$ (dl / g)
—**	74.5	1481	1.40	0	0
THF	68.0	2700	1.60	82.3	0.20
ETH	66.5	2760	1.50	86.4	0.10
DME	74.5	2960	1.55	99.9	0.15
2G	73.9	3131	1.52	111.4	0.12

* Based on optimum ether / Al mole ratio

Polymerization conditions:

V / P = 4.5×10^{-4} , $t = 3.5h$, others are the same as that in Table 1.

** V / P = 9.5×10^{-4}

It could be seen from the data in Table 5 that, when optimum ether / Al mole ratio was used for each ether not only could the catalytic efficiency doubled but the $[\eta]$ of the obtained copolymer could be increased to some extent.

2. The activation effect of ether on $VO[OCH_2C(CH_3)_3]_2 Cl-Al i Bu_3$ system

(1) The stabilization effect of ether on V^{+3}

It had been proved that V^{+3} complex was the active center in $VO[OCH_2C(CH_3)_3]_2 Cl-Al i Bu_3$ system^[3]. To understand the activation effect of ether the first thing should be done was to check the effect of ether (DME was used as a representative here) on $V^{+3}\%$. Therefore potential titration method was used to measure the variation of the valence state of vanadium ion with time, with or without DME in the catalyst system (Table 6).

Table 6 The changes of the valence state of vanadium ion with time

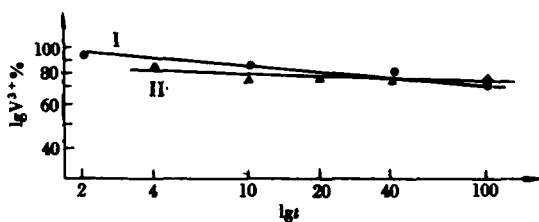
	Reaction time (min.)	V ⁺² (%)	V ⁺³ (%)	Average valence state
Without DME	2	6.8	93.3	2.93
	10	16.5	83.5	2.84
	40	21.4	78.6	2.79
	100	28.9	71.1	2.71
DME / Al = 0.025	4	14.6	85.4	2.85
	10	25.3	74.7	2.75
	20	22.5	77.5	2.78
	40	23.2	76.8	2.77
	100	25.5	75.5	2.76

Measurement conditions: $[V] = 0.03 \text{ mM/ml}$, $Al/V = 16$, $T = -45^\circ\text{C}$.

It could be seen from the variation of $V^{+3}\%$ in Table 6 that if there was no DME in the system $V^{+3}\%$ decreased by 22% and the average valence state of vanadium ion decreased by 0.22 when the time for V and Al to contact each other lasted from 2 min. to 100 min.; while with DME on the system, during the same time period $V^{+3}\%$ decreased only by 10% and the average valence state of vanadium ion by 0.09. This indicated that the function of DME was to stabilize V^{+3} and prevent it from being further reduced to V^{+2} ion. The degree of reduction could be characterized by the slope of the straight line in Fig.1 which was plotted through bilogarithmic coordinate of $V^{+3}\%$ vs. reaction time. There was not too much difference in slopes of two straight lines. It indicated that the stabilizing effect of DME on V^{+3} active center was limited.

(2) The nature of interaction between ether(DME) and V^{+3}

In order to understand the nature of the interaction between DME and V^{+3} , the UV-VIS and IR spectrometers were used to record the VIS spectra of the hydrolysis products of the V-Al catalyst systems, with or without DME in the system(Fig.2) and IR spectra of the mixtures(Fig.3)

Fig.1 The relationship between $V^{+3}\%$ and reaction time

I. without DME; II. DME / Al = 0.025

The $\lambda_{\max}$ of characteristic peaks of V^{+2} (560 nm), V^{+3} (480 and 625 nm) and V^{+4} (650 nm) in Fig.2 were substantially in good agreement with those in references^[6-8], but the position of the peak ($\lambda_{\max}$, curve I) characterized V^{+3} shifted to the direction of short wavelength after DME was added into the catalyst system. It indicated that with DME involved the field intensity of the ligands of V^{+3} increased which showed that there did exist the interaction between DME and V^{+3} and it accounted for the stabilization of V^{+3} . It could be seen from Fig.3 that after the addition of DME into the

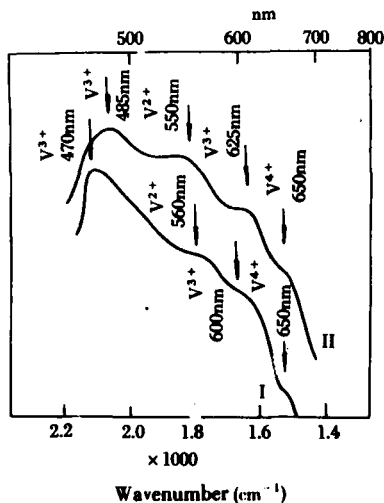


Fig.2 VIS spectra of the hydrolysis product of the catalyst systems

I. DME/Al = 0.0025; II. Without DME

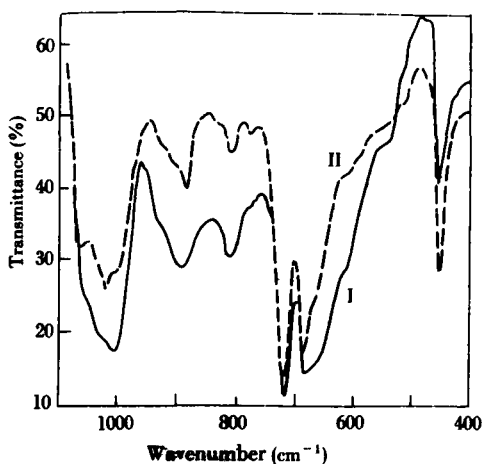
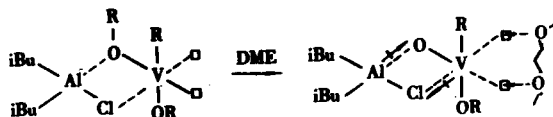


Fig.3 IR spectra of V-Al(I) and V-Al-DME(II) systems

catalyst system (curve II) the intensity of the absorption peak (610 cm^{-1}) which characterized the vibration of $\text{Al} \rightarrow \text{O}$ bond weakened obviously while the intensity of the absorption peak (450 cm^{-1}) which characterized the vibration of $\text{V}-\text{Cl}$ bond increased to some extent. This might be due to the fact that the oxygen atom of DME coordinated weakly with V^{+3} at the vacancy of active center thus causing the variation of the charge distribution of the chemical bond, i. e. the instantaneous dipole moment of $\text{V}-\text{Cl}$ increased and the instantaneous dipole moment of $\text{Al} \rightarrow \text{O}$ decreased.

In addition, it was observed that when the feeding order of $\text{Bd} + \text{P} + \text{V} + \text{DME} + \text{Al}$ was adopted, after vanadium compound was added into the toluene solution of the monomers the solution appeared light yellow. DME solution was added into above solution which deepened obviously and showed bright yellow. In the field of coordination chemistry of transition metal the change of color more often than not reflects the variation of intensity of ligand field and active center ion.

According to above measurement and observation the mechanism of the interaction between DME and V^{+3} active center was proposed:



When Bd was present in the system there was some competition between DME and Bd for coordination.

(3) The interaction between DME and $\text{Al}(\text{iBu})_3$

The IR spectra of $\text{Al}(\text{iBu})_3$, DME and the mixture of $\text{Al}(\text{iBu})_3$ -DME were recorded separately. The results showed that after the adding of $\text{Al}(\text{iBu})_3$ the intensity of the absorption peak (1080 cm^{-1}) which characterized the vibration of ether bond in DME weakened considerably which implied that there was interaction between DME and $\text{Al}(\text{iBu})_3$, but the nature of the interaction and the pattern of the complex could not be drawn positively from the presented data.

3. The effect of ether on temperature-sensitivity of V-Al system

There were two purposes in adding ether additives into V-Al system. First, attempt to increase the concentration and lifetime of V^{+3} through some kind of complex effect so that the catalytic activity could be increased. The above experimental data had demonstrated that this attempt was realized to some extent. Secondly, it was expected that the interaction between V^{+3} and ether could stabilize V^{+3} so that the temperature-sensitivity of the catalyst system could be decreased and the polymerization temperature could be raised. Therefore the comparison experiments of increasing polymerization temperature were carried out and the result is shown in Fig.4 and Table 7.

Table 7 The effect of polymerization temperature on conversion and $[\eta]$ of copolymer in V-Al-ether system

Polymerization temp.(°C)	DME / Al = 0.025		2C / Al = 0.020	
	conversion(%)	$[\eta]$ (dl/g)	conversion(%)	$[\eta]$ (dl/g)
-45	97.3	1.45	88.6	1.40
-30	66.3	1.18	64.8	1.18

Polymerization conditions: the same as that in Table 3 except for polymerization temperature.

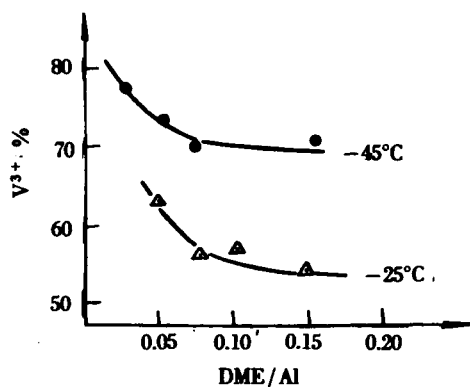
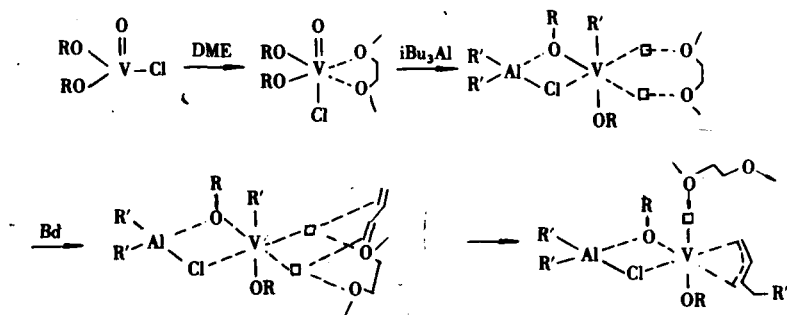


Fig.4 The effect of DME/Al mole ratio on $V^{+3}\%$ under various temperatures

Experimental results indicated that when the polymerization temperature was raised from -45°C to -25°C not only V^{+3} content decreases but the optimum DME/Al mole ratio increases (Fig.4), and at the same time the corresponding conversion decreases from 90% to 65%. It could be reasoned that it was possible that there was some kind of interaction between ether and V^{+3} active center which functioned to stabilize V^{+3} . But at low temperature this kind of coordination was not strong enough to affect the coordination of monomer to increase the activity of the catalyst system. When temperature was raised this weak function of coordination stabilization was further weakened and even disappeared, so it was still impossible to improve the temperature-sensitivity of V-Al system.

According to the preceding measurement and experimental data it was assumed that the weak coordination complex was formed from ether (DME was used as an example) and V^{+3} active center in the following pattern:



where $R' = iBu$. According to the theory of coordination field the normal octahedron complex with two vacancies is not stable and has the tendency to rearrange to double triangle cone. In order to explain the possibility of the existence of normal octahedron complex with two vacancies it was often assumed that the vacancies were occupied temporarily by solvent molecules. After the addition of ether the solvent molecules were replaced by oxygen atoms with a pair of unbounded electrons and the weak coordination complex with V^{+3} was formed at the place of vacancy. In this case the positive charge of V^{+3} was decreased, so it was stabilized at high valence state. But this effect was not enough to influence the coordination of Bd or P, therefore the increase in the number of stabilized V^{+3} resulted in the increase in catalytic activity. Above diagram also indicated that DME could only function to stabilize V^{+3} but could not restrain the termination reaction of growing chain caused by monomer transfer or β -H transfer. Therefore the experimental fact that both the $[\eta]$ of copolymer and polymerization temperature were not obviously increased was explained.

Keywords:

Additives, butadiene-propylene alternating copolymer, vanadium-aluminum catalyst, catalytic efficiency

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