

Improved Coordination Catalyst for the Alternating Copolymerization of Butadiene and Propylene*

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Synopsis

A close reexamination of previously reported vanadium-based catalysts for the alternating copolymerization of butadiene and propylene resulted in an improved catalytic system for the above reaction. We found the system $\text{VO}(\text{OR})_2\text{Cl}/i\text{-Bu}_3\text{Al}$ where R is neopentyl to be most effective. Qualitative relationships between the structure of the alkyl residue in $\text{VO}(\text{OR})_2\text{Cl}$ and the catalyst efficiency have been elaborated. High-molecular-weight copolymers of butadiene and propylene, which consist of a perfectly alternating sequence of *trans*-1,4-butadiene and propylene units, are obtained.

INTRODUCTION

Alternating copolymers of butadiene and propylene (BPR) have been reported first in 1969 by Furukawa¹ (Fig. 1).

More recently, improved catalysts for the preparation of BPR were introduced^{2,3} (Table I).

Both titanium- and vanadium-based catalytic systems exhibit activities too low for technical applications (50 mmole transition metal compound per kg copolymer). The titanium-based catalyst generates copolymers of high molecular weight, but with low stereospecificity.^{4,5} On the other hand, vanadium catalysts provide the desired high steric purity, but the products have molecular weights too low (<100,000) with respect to technical applications.

This article deals with vanadium catalysts of improved efficiency for the alternating copolymerization of butadiene and propylene.

EXPERIMENTAL

All polymerization procedures were performed under a dry atmosphere of nitrogen. Solvents were dried by azeotropic distillation. Butadiene was of polymerization grade and used without further purification. Propylene was passed through a 2-m column packed with 4 Å molecular sieves. Aluminumalkyls were commercially available and used as molar solutions in *n*-hexane or toluene. Vanadium compounds were prepared by reacting VOCl_3 with two

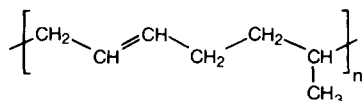


Fig. 1. Structure of BPR.

* Dedicated to Prof. Dr. H. Gr \ddot{u} newald on the occasion of his 60th birthday.

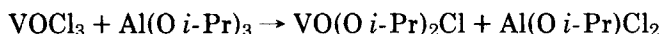
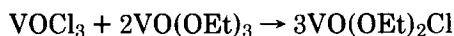
TABLE I
 Catalysts for the Preparation of BPR

Catalyst No.	Catalyst	Reference
1	$\text{VCl}_4 + \text{Et}_3\text{Al}$ 1 : 3	1
2	$\text{VO}(\text{acac})_2 + \text{Et}_3\text{Al} + \text{Et}_2\text{AlCl}$ 1 : 3 : 1	1
3	$\text{VOCl}_3 + \text{VO}(\text{OEt})_3 + i\text{-Bu}_3\text{Al}$ 0.4 : 0.6 : 2.5	2
4	$\text{TiCl}_4 + \text{C}_6\text{H}_5\text{COCH}_3 + i\text{-Bu}_3\text{Al}$ 1 : 1 : 3	2
5	$\text{VOCl}_3 + \text{Al}(\text{O } i\text{-Pr})_3 + i\text{-Bu}_3\text{Al}$ 1 : 2.5 : 10	3

equivalents of an alcohol, the reaction being monitored by measuring the amount of HCl evolved. Further experimental details have been described elsewhere.⁶

RESULTS AND DISCUSSION

Considering the vanadium catalysts 3 and 5 of Table I, which, like the others, have to be preformed at very low temperatures (-70°C), one can assume a ligand exchange to take place, both yielding $\text{VO}(\text{OR})_2\text{Cl}$ according to the following equations:



Consequently, we prepared a number of dialkoxivanadium oxichlorides and examined their activity as catalyst components. The results are listed in Table II. The results given in the table show an unexpected and striking dependence of catalyst activity on structural changes in the alkoxy ligands of $\text{VO}(\text{OR})_2\text{Cl}$. We find that catalyst activity varies with the bulkiness and position of substituents in the alkyl chain of R. If R is an *n*-alkyl residue, then the catalyst is almost inactive under the polymerization conditions (catalysts 1, 3, 9, and 16). α Branching results in a slight increase in activity (catalysts 2, 4, 6, and 11), the latter being further enhanced by β substitution (catalysts 5, 7, 12, 14, and 15). By introducing two substituents at the β -carbon atom of R, the catalyst activity is enhanced considerably (10), whereas substitution in γ position remains ineffective (8 and 11). The neopentyl residue exhibits a remarkable activity. The influence of the organoaluminum compound employed is shown in Table III.

Only aluminumtrialkyls are suitable, higher alkyls being more efficient than lower ones. Interestingly, again the branched alkyl residue exhibits the highest activity. In contrast to earlier findings,¹⁻³ our catalyst $\text{VO}[\text{OCH}_2\text{C}(\text{CH}_3)_3]_2\text{Cl}/i\text{-Bu}_3\text{Al}$ loses activity upon preforming at -78°C .

TABLE II
Influence of R in VO(OR)₂Cl on Catalyst Activity^a

Catalyst No.	R	Conversion, %	Catalyst No.	R	Conversion, %
1	CH ₃ —CH ₂ —CH ₂ —	0	9	CH ₃ —CH ₂ —CH ₂ —CH ₂ —CH ₂ —	0
2		1.2	10		80
3	CH ₃ —CH ₂ —CH ₂ —CH ₂ —	0	11		1.6
4		8.2	12		14.7
5		7.7	13		0
6		1.6	14		9.8
7		9.8	15		23
8		0	16	CH ₃ —(CH ₂) ₆ —CH ₂ —	0

^a Polymerization conditions: molar ratio butadiene/propylene = 1:1; monomer concentration, 31 wt % in *n*-hexane; reaction temperature, -50°C; catalyst, 0.8 mmole VO(OR)₂Cl phm, 5.0 mmole *i*-Bu₃Al phm; reaction time, 3 hr.

The great difference in catalyst activity is probably due to steric interactions exerted by the various alkoxy ligands in VO(OR)₂Cl. This can be illustrated by dynamic ¹H-NMR spectroscopy (DNMR spectroscopy) (Figs. 2 and 3).

TABLE III
Influence of Aluminum Compound^a

Al compound	Conversion, %	[η], dl/g toluene, 25°C
Me ₃ Al	<5	—
Et ₃ Al	5.2	0.88
<i>n</i> -Bu ₃ Al	17	1.05
<i>i</i> -Bu ₃ Al	66	1.25
Oct ₃ Al	29	1.20
<i>i</i> -Bu ₂ AlH	—	—
Et ₂ AlCl	—	—
Et ₂ AlBr	—	—
<i>i</i> -Bu ₂ AlCl	—	—
Et ₂ AlOEt	—	—
Et ₃ Al ₂ Br ₃	—	—

^a Polymerization conditions: molar ratio butadiene/propylene = 1:1; monomer concentration, 20 wt % in toluene; catalyst, 0.8 mmole VO[OCH₂C(CH₃)₃]₂Cl phm, 5 mmole Al compound phm; reaction time, 4 hr; reaction temperature, -45°C.

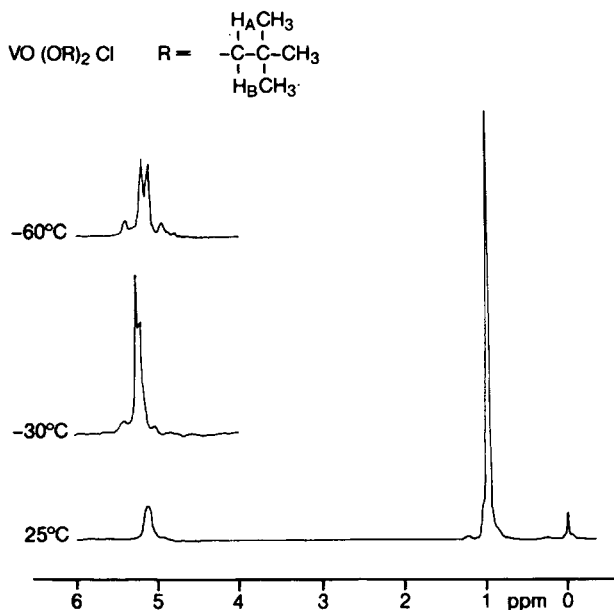


Fig. 2. DNMR spectroscopy of $\text{VO}[\text{OCH}_2\text{C}(\text{CH}_3)_3]_2\text{Cl}$.

Figure 2 shows the spectrum for $\text{R} = \text{neopentyl}$. The α -methylene protons appear as a broadened singlet at $\delta = 5.17$ ppm, which splits off into an AB quartet upon cooling. This indicates a restricted rotation of the methylene group as a consequence of steric hindrance effected by the adjacent *tert*-butyl moiety.

Figure 3 shows the corresponding spectrum for $\text{R} = 2\text{-methylbutyl}$. The doublet of the α -methylene protons at $\delta = 5.28$ ppm collapses at -60°C to a broad peak, thus indicating a less hindered rotation than in the preceding case, as is expected, if the steric influence of the adjacent *sec*-butyl moiety is considered. However, other explanations can be discussed.⁷

The molecular weights of the copolymers are controlled by the reaction temperature (Table IV). Mooney viscosities ($\text{ML } 1 + 4/100^\circ\text{C}$) of 50 are obtained at $\sim -45^\circ\text{C}$.

TABLE IV
Dependence of Molecular Weights on Reaction Temperature^a

T , $^\circ\text{C}$	$[\eta]$, dl/g toluene, 25°C	ML $1 + 4/100^\circ\text{C}$	$M_w \times 10^{-3}$
-20	0.81	—	55
-30	0.99	10	70
-40	1.25	28	130
-50	1.48	56	175
-55	1.62	63	200
-60	1.73	70	240

^a Polymerization conditions as in Table III, with *i*- Bu_3Al as aluminum compound.

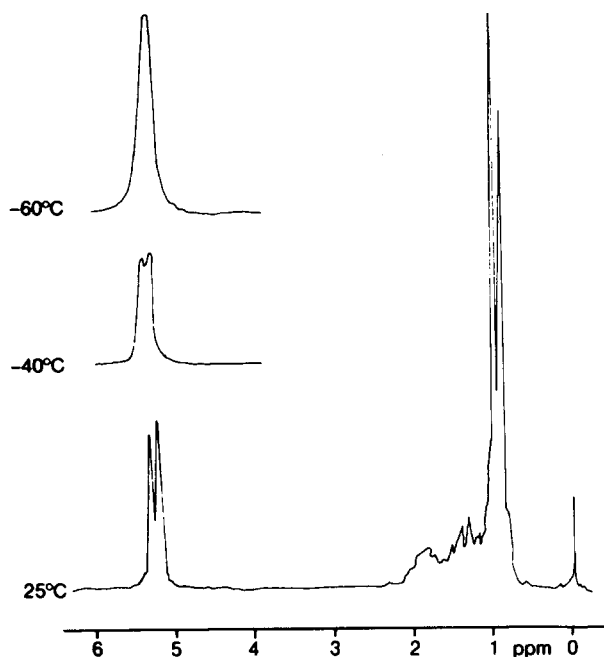
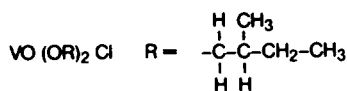
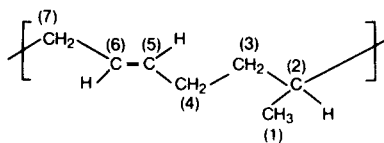


Fig. 3. DNMR spectroscopy of $\text{VO}[\text{OCH}_2\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5]_2\text{Cl}$.

In accordance with earlier investigations,³ the molecular structure of the material is very regular. The repeating unit consists of a *trans*-1,4-butadiene and a propylene monomer, according to ^{13}C -NMR measurements. The assignment of the chemical shifts is given in Figure 4.



C-atom Nr.	δ (ppm)
1	19.337
2	32.624
3	36.507
4	30.184
5	131.682
6	128.424
7	39.957

Fig. 4. Assignment of ^{13}C -shifts δ (ppm, TMS = 0) in $\text{CDCl}_3/\text{CCl}_4$.

CONCLUSIONS

With the catalyst $\text{VO}[\text{OCH}_2\text{C}(\text{CH}_3)_3]_2\text{Cl}/i\text{-Bu}_3\text{Al}$, stereoregular, high-molecular-weight alternating copolymers of butadiene and propylene were prepared in high yields. The catalyst efficiency is reasonable high for technical use (3–5 mmole vanadium compound per kg copolymer). Characterization and properties of the material will be communicated in a subsequent report.

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