Polymer Vol. 37 No. 2, pp. 363–365, 1996
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0032-3861/96/$15.00+0.00

Polymerization of 1,3-dienes with catalysts based on mono- and bis-cyclopentadienyl derivatives of vanadium

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(Received 24 March 1995)

Butadiene, 1,3-pentadiene, 2-methyl-1,3-pentadiene and 4-methyl-1,3-pentadiene have been polymerized with MAO/Cp′$VCl_2 \cdot 2PEt_3$ and MAO/Cp_2VCl (Cp′ = C_5H_4Me, Cp = C_5H_5). Polymers, predominantly *cis*-1,4, have been obtained from butadiene and pentadiene, a polymer with a mixed *cis/trans* structure has been obtained from 2-methyl-1,3-pentadiene, while 4-methyl-1,3-pentadiene gave a predominantly 1,2 polymer. Cp′$VCl_2 \cdot 2PEt_3$/MAO was found to be particularly active. The different stereospecificities of the systems are discussed with respect to other soluble vanadium systems.

(Keywords: diolefin polymerization; vanadium catalysts; *cis*-1,4 polybutadiene)

Introduction

Various catalyst systems based on vanadium are active for the polymerization of conjugated diolefins[1]. The heterogeneous systems, derived from VCl_3, VCl_4 or $VOCl_3$ and aluminium-alkyls (AlR_3, AlR_2Cl; R = alkyl group), yield polymers with a *trans*-1,4 structure from butadiene, isoprene and various terminally substituted diolefins.

Soluble vanadium catalysts derived from $V(acac)_3$ or $VCl_3 \cdot 3THF$ and AlR_3 or $AlEt_2Cl$ have also been used. The soluble systems containing Cl atoms (e.g. $AlEt_2Cl$–$V(acac)_3$; $AlEt_2Cl$–$VCl_3 \cdot 3THF$) give *trans*-1,4 polymers from butadiene and isoprene and polymers with a mixed *trans*-1,4/1,2 structure from pentadiene[1].

Recently, it has been reported that the soluble system MAO/$V(acac)_3$ also gives *trans*-1,4 polymers from butadiene and other diolefins[2,3].

The high tendency of vanadium systems to give polydiolefins with a *trans*-1,4 structure has been attributed to an *anti* → *syn* isomerization of the η^3-allyl group that occurs during polymerization[3].

We have now examined the polymerization of some diolefins with homogeneous systems $(\eta^5\text{-}C_5H_4Me)VCl_2 \cdot (PEt_3)_2$/MAO and $(\eta^5\text{-}C_5H_5)_2VCl$/MAO. These systems, unlike the other known chlorine-containing soluble vanadium systems, give diolefin polymers with a predominantly *cis*-1,4 structure. In addition, $(\eta^5\text{-}C_5H_4Me)VCl_2 \cdot (PEt_3)_2$ has been found to be much more active than the other soluble vanadium systems so far proposed. This note reports on the most significant polymerization results obtained with the above two catalysts, and on a possible interpretation.

Experimental

Materials. Triacetylacetonatovanadium ($V(acac)_3$) (Aldrich, > 97% pure) and methylaluminoxane (MAO) (Witco, 30 wt% solution in toluene) were used without further purification. $(C_5H_4Me)VCl_2 \cdot (PEt_3)_2$ and Cp_2VCl were prepared according to literature procedure[4,5]. Toluene (Baker, > 99% pure) was refluxed over Na for 8 h, then distilled and stored over molecular sieves under dry nitrogen. Butadiene (Enichem Elastomeri, > 99.5% pure) was evaporated from the container prior to each run, dried by passing through a column packed with molecular sieves and condensed into the reactor which was precooled to −20°C. Isoprene (Enichem Elastomeri, > 99.5% pure), (E)-1,3-pentadiene (Aldrich, 98% pure), (Z)-1,3-pentadiene (Fluka, > 98% pure), (E)-2-methyl-1,3-pentadiene (Fluka, > 98% pure) and 4-methyl-1,3-pentadiene (Fluka, > 98% pure) were refluxed over CaH_2 for about 2 h, then distilled trap-to-trap and stored under dry nitrogen.

Polymerization. The polymerization of butadiene reported in *Table 1*, run 1, is reported as a standard procedure. The monomer (10 ml) was introduced into a 250 ml glass reactor, toluene (80 ml) was added and the solution was brought to the desired temperature (15°C); MAO (1×10^{-2} mol) and the vanadium compound (1×10^{-5} mol) were added in this order. The polymerization was terminated with methanol, the polymer was coagulated and repeatedly washed with methanol, then dried in vacuum at room temperature.

All the other polymerization runs were carried out in a similar way. When preformed catalysts were used (*Table 1*, runs 7 and 8), the monomer was added at the end.

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Table 1 Polymerization of butadiene with catalysts based on cyclopentadienyl derivatives of vanadium[a]

	Catalyst			Polymerization			Polymer			
Run	V-compound	mol × 10^5	Al/V	Temp. (°C)	Time (min)	Conv. (%)	*cis*-1,4 (%)	*trans*-1,4 (%)	1,2 (%)	$[\eta]$[c] ($dl\,g^{-1}$)
1	$Cp'VCl_2 \cdot (PEt_3)_2$	1	1000	15	5	81.5	80.4	2.4	17.2	3.3
2	$Cp'VCl_2 \cdot (PEt_3)_2$	1	100	15	60	38.4	82.4	2.1	15.5	1.4
3	$Cp'VCl_2 \cdot (PEt_3)_2$	1	1000	−30	60	26	81.6		18.4	
4	Cp_2VCl	2	1000	15	56	40	84.8	1.8	13.4	ins
5	Cp_2VCl	2	1000	−30	310	6	88.9		11.1	
6	Cp_2VCl	5	100	15	305	8	87.2	1.1	11.7	
7[b]	Cp_2VCl	5	100	15	131	11.8	87.7	1.3	11	
8[b]	Cp_2VCl	1.5	100	15	26	22	90	2	8	
9	$V(acac)_3$	1	1000	15	15	47		100		3.2

[a] Polymerization conditions: toluene, 80 ml; monomer, 10 ml

[b] In these runs catalysts preformed and aged at 15° C for 120 min were used (in the presence of a small amount of butadiene ($C_4H_6/V = 10$ molar ratio) in run 8)

[c] Intrinsic viscosity, determined in toluene at 25° C

Table 2 Polymerization of some diolefins with catalysts based on cyclopentadienyl derivatives of vanadium[a]

		Catalyst			Polymerization			Polymer		
Run	Monomer	V-compound	mol × 10^5	Al/V	Temp. (°C)	Time (h)	Conv. (%)	*cis*-1,4 (%)	*trans*-1,4 (%)	3,4 (%)
1	isoprene	$Cp'VCl_2 \cdot (PEt_3)_2$	1	1000	25	5	75.6	78.2		21.8
2	isoprene	$Cp'VCl_2 \cdot (PEt_3)_2$	1	1000	0	1	16.9	83		17
3	isoprene	$Cp'VCl_2 \cdot (PEt_3)_2$	3	1000	−30	143	27.2	83		17
4	isoprene	Cp_2VCl	4	500	25	24	7	82.1		17.9
5	(E)-1,3-pentadiene	$Cp'VCl_2(PEt_3)_2$	1	1000	0	4	22.7	71		29[b]
6	(Z)-1,3-pentadiene	$Cp'VCl_2(PEt_3)_2$	4	500	20	116	11.4	85	15	
7	(E)-2-methyl-1,3-pentadiene	$Cp'VCl_2(PEt_3)_2$	4	500	−30	119	20	50	50	
8	4-methyl-1,3-pentadiene	$Cp'VCl_2(PEt_3)_2$	4	1000	−30	68	33.8		18	82[b]

[a] Polymerization conditions; monomer, 2 ml; toluene, 16 ml

[b] 1,2 units

Polymer characterization. Intrinsic viscosities were determined in toluene at 25°C using a Desreux-Bishof viscometer. ^{13}C n.m.r. examination was performed on a Bruker AM 270 instrument. The spectra were obtained in $C_2D_2Cl_4$ at 110°C (HMDS as internal standard) or in $CDCl_3$ (TMS as internal standard). The concentration of the polymer solution was about 10 wt%. Infra-red spectra of the polymers were taken on a Perkin Elmer 457 IR Grating Spectrophotometer, using films on KBr discs. Polymer microstructure was determined as reported in the literature[6–10].

Results and discussion

Polymerization results on butadiene and other conjugated diolefins with $Cp'VCl_2 \cdot (PEt_3)_2/MAO$ ($Cp' = C_5H_4Me$) and Cp_2VCl/MAO ($Cp = C_5H_5$) are reported in *Tables 1* and *2*.

$Cp'VCl_2 \cdot (PEt_3)_2$ was used because $Cp'VCl_2$ is unstable at room temperature, and disproportionates[4] according to the equation:

$$2Cp'VCl_2 \rightarrow Cp'_2VCl + VCl_3$$

It is stable, however, when complexed with PMe_3 or PEt_3.

We have used the compound containing the Cp′ group and PEt_3 for catalyst preparation because of its higher solubility with respect to that containing Cp group and PMe_3[4].

The activity of $Cp'VCl_2 \cdot 2PEt_3/MAO$ depends on the Al/V molar ratio (*Table 1*, runs 1 and 2). A comparison of the activity of these systems with that of MAO/$V(acac)_3$ (run 9), one of the most active vanadium catalysts so far known, shows that the $Cp'VCl_2$ catalyst is more active by a factor of around 6, in the polymerization of butadiene.

Unlike the other known vanadium catalysts, which were characterized by a *trans* stereospecificity[1], the $Cp'VCl_2$ system gives polybutadiene with predominantly *cis* structure (~ 80%, the remaining units being predominantly 1,2), independently of the polymerization temperature and Al/V molar ratio.

In a recent paper[3], we have attributed the formation of *trans* polymers with MAO/$V(acac)_3$ to an *anti* → *syn* isomerization of the η^3-butenyl group during polymerization. Various pieces of evidence indicate that the formation of *trans* vs. *cis* units with most of the soluble transition metal catalysts depends on the relative rate of two processes: (a) *anti* → *syn* isomerization of the η^3-allyl group; (b) incorporation of the coordinated monomer. The different stereospecificity of the $V(acac)_3$ systems and of the systems of this note may be explained assuming that the isomerization is slower than monomer incorporation with the latter systems, whereas the opposite occurs with $V(acac)_3/MAO$.

Polymerization results for isoprene, (Z)- and (E)-1,3-pentadiene, (E)-2-methyl-1,3-pentadiene and 4-methyl-1,3-pentadiene with $MAO/Cp'VCl_2 \cdot (PEt_3)_2$ are reported in *Table 2*. The amount of polymer obtained from each of these monomers is much lower than that obtained from butadiene. The polymers have, however, a predominantly *cis*-1,4 structure, with the exception of those obtained from (E)-2-methyl-1,3-pentadiene (50% *cis*; 50% *trans*) and 4-methyl-1,3-pentadiene (82%1,2).

Cp_2VCl/MAO yields the same stereospecificity as $Cp'VCl_2 \cdot (PEt_3)_2/MAO$ in the polymerization of butadiene (polymers with a very low molecular weight or oligomers were obtained from the other diolefins); its activity is, however, much lower. Also in this case the activity increases with increasing the Al/V molar ratio, being significantly higher at Al/V = 1000 than that at Al/V = 100.

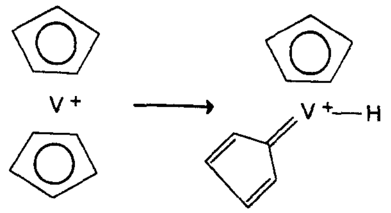
We have examined the effect of ageing on catalyst activity with catalysts prepared at Al/V = 100 (*Table 1*, runs 7 and 8). Ageing the catalyst in the absence of monomer has a modest effect on activity (run 7), but when the catalyst is aged in the presence of a small amount of monomer (run 8), a pronounced enhancement of the activity is observed. This experiment indicates that the formation of the active species, at Al/V = 100, is slow. The fact that the enhancement of activity is higher when the catalyst is aged in the presence of the monomer can be interpreted as follows: in the absence of monomer, V–Me bonds are formed; these are transformed into (η3-allyl)–V bonds in the presence of the monomer. It is known that (η3-allyl)–V bonds are more stable than V–C bonds of σ type, and this probably explains our results.

The systems derived from $Cp'VCl_2 \cdot 2PEt_3$ and Cp_2VCl have most probably an ionic structure, as have those derived from Cp derivatives of Ti and Zr. The active species in the $Cp'VCl_2 \cdot 2PEt_3$ system presumably contains the cation $[CpV\text{-}Me]^+$. In the case of the Cp_2VCl system, presumably the following reactions take place:

$$Cp_2VCl + MAO \rightarrow Cp_2VMe$$

$$Cp_2VMe + MAO \rightarrow [Cp_2V]^+[MAOMe]^-$$

The cation $[Cp_2V]^+$ does not contain V–C bounds of σ type. Its activity may be accounted for by assuming that it disproportionates as follows:



A disporportionation of this type has been demonstrated for Cp_2Ti (ref. 11). The V–C bond active in the polymerization is formed by reaction of the monomer with the V–H bond.

Conclusions

We have examined the polymerization of some 1,3-dienes with catalysts derived from cyclopentadienyl derivatives of vanadium, in combination with MAO; catalysts of this type had not been used previously for the polymerization of this class of monomers. The main features of these catalysts are as follows:

(1) they give polymers with a predominantly *cis*-1,4 structure, while the vanadium catalysts so far known give predominantly *trans*-1,4 or 1,2 polymers;
(2) the catalyst from $CpVCl_2$ is significantly more active than that from Cp_2VCl; in addition, it is more active than the vanadium catalysts previously proposed for the polymerization of dienes. We have not investigated whether the higher activity of the $CpVCl_2$ catalyst may depend on a higher number of active centres or a higher value of the kinetic constant K_p, or on both.

Finally, we have proposed that in the active species of the Cp_2VCl catalyst, one Cp group assumes a carbene-like structure to produce an ionic species.

Acknowledgements

We wish to thank Mr Salvatore Italia for technical assistance.

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