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Diolefin polymerization by half-sandwich complexes and MAO as cocatalyst

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Abstract

Different half-sandwich titanium trifluorides and constrained geometry catalysts of titanium and vanadium were used to polymerize butadiene, isoprene, and 1,3-pentadiene. The polybutadienes produced with these catalysts have nearly identical microstructures of about 80% 1,4-*cis*, 1% 1,4-*trans* and 19% 1,2-linked units. An optimum activity is obtained by an aluminium/titanium ratio of about 700. There is no dependence of the aluminium/titanium ratio on the microstructure. Vanadium-based complexes are more active for 1,3-pentadiene than titanium complexes. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polydienes; Polybutadiene; Metallocene catalysts

1. Introduction

Metallocene/methylaluminoxane (MAO) catalysts are able to polymerize 1,3-butadiene and to copolymerize ethene and 1,3-butadiene [1,2]. Porri and Oliva [3–6] demonstrated that cyclopentadienyl titanium trichloride in combination with MAO is able to polymerize 1,3-butadiene to a rubber with a high content of *cis*-1,4- and 1,2-units but a low content of *trans*-1,4-units.

We have shown that alkylsubstituted cyclopentadienyl titanium trifluorides and trichlorides (Fig. 1) are more temperature stable and very active for the homogeneous polymerization of styrene and dienes [7–10]. Especially the 1,3-dimethylcyclopentadienyl titanium compound shows the highest activity (Table 1). Surprisingly, high molecular weights are obtained for the polybutadienes produced with these catalysts.

The di- and trimethylcyclopentadienyl titanium trichlorides give the highest molecular weights up to 3 million, while the fluorinated compounds have significantly lower molecular weights, even if their activity is higher.

For all catalysts, the 1,4-*cis* structure units of the polybutadiene range between a content of 74 and 85.8%, the 1,4-*trans* between 0.5 and 4.2%, and the 1,2-units between 13.7 and 22.6%. The most active systems generate the polymer with the highest content of *cis*-1,4 and the lowest content of 1,4-*trans* and 1,2-units. Chlorinated and fluorinated catalysts produce polymers with a similar microstructure. An explanation for the differences between the mechanism of polymerization of 1,3-dienes and olefins is given by Porri [11]. One difference relates to the type of bond between the transition metal of the active species and the growing polymer chain. There is an η^3-allyl bond in diene polymerization and a σ-type bond in propene polymerization. Owing to this difference, the factors determining or affecting activity and stereospecificity are different. Another difference concerns the mode of coordination of the two classes of monomers. A 1,3-diene can coordinate *cis*-η^4, *trans*-η^4 or *trans*-η^2. In most cases, the *cis*-η^4 is energetically favoured.

Polymerizations of 1,3-butadiene with silica-supported $CpTiCl_3$/MAO in a stirred bed reactor or a fluidized bed reactor increase the activity but produce partly insoluble polymers. The polybutadienes produced in the gas phase have similar characteristics in the fluidized bed polymerization as in the homogeneous process.

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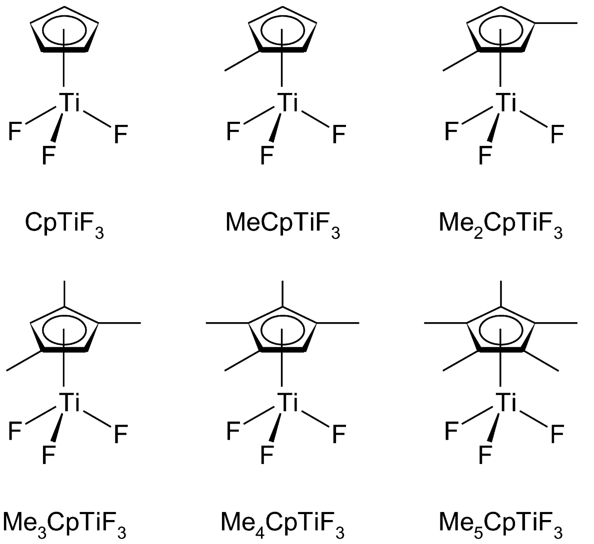

Fig. 1. Structures of different methyl substituted cyclopentadienyl titanium trichlorides. Trichlorides similar.

2. Experimental part

2.1. Materials

All reaction steps were carried out in an argon atmosphere using Schlenk techniques. Toluene and other solvents were dried over a sodium/potassium alloy and distilled before use. 1,3-Butadiene was purchased from Gerling Holz, and purified by passing it through columns containing molecular sieves and active Al_2O_3, MAO, TIBA and the constrained geometry catalysts were purchased from Witco and used as received. The different substituted cyclopentadienyl trichlorides and trifluorides were prepared in our laboratory according to the processes described in the literature [12,13]. $[Me_2Si(N^tBu)(Me_4Cp)]VCl_2$ (Fig. 2) was prepared as described in the literature [14].

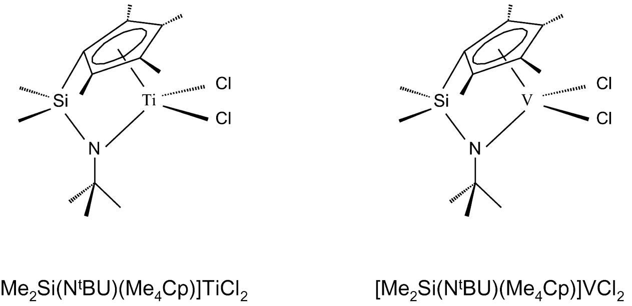

Fig. 2. Structures of [(^{t}butylamido)-dimethylsilylene-2,3,4,5-tetramethyl-cyclopentadienyl]titanium dichloride $[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2$ and the analogue $[Me_2Si(N^tBu)(Me_4Cp)]VCl_2$.

$Cp'VCl_2$ ($H_2Cp' = C_5Me_4H(SiMe_2NH^tBu)$) was prepared by a modified procedure for the synthesis of $C_5Me_5VCl_n$ [14]: 2.3 g (9 mmol) of H_2Cp' were dissolved in 10 ml of absolute THF. Sodium sand (0.46 g, 20 mmol) was added, and the suspension was stirred for 1 day at 50 °C (solution I). VCl_3 (1.67 g, 10 mmol) was dissolved in 40 ml of THF and stirred overnight (solution II). Solution II was warmed to 60 °C, and solution I was added in three portions after 30 min intervals to yield a dark red solution. After 2 days of stirring at 60 °C, the colour changed to brown due to the formation of $Cp'VCl_2$. The solution was then filtered, concentrated to one-third of its original volume, and allowed to stand at 4 °C for a couple of hours. Excess $VCl_3(THF)_3$ crystallized and was filtered off. This procedure was repeated two to three times, until removal of the major part of the $VCl_3(THF)_3$. Evaporation of the filtrate and drying of the residue under vacuum finally yielded brown, solid $Cp'VCl_2$.

Table 1
Activities, microstructures and glass transition temperatures of polybutadienes produced by half-sandwich titanocenes by 30 °C in 100 ml toluene, 10 g 1,3-butadiene, 0.29 g MAO, $[Ti] = 5 \times 10^{-5}$ mol/l, 20 min

Catalyst	Activity[a]	1,4-*cis* (%)	1,4-*trans* (%)	1,2 (%)	T_g (°C)
$CpTiCl_3$	260	81.7	1.1	17.2	−95.1
$MeCpTiCl_3$	300	81.9	1.1	17.0	−95.3
$Me_2CpTiCl_3$	750	85.8	0.5	13.7	−96.9
$Me_3CpTiCl_3$	340	83.8	1.1	15.2	−95.6
$Me_4CpTiCl_3$	165	80.0	1.7	18.3	−91.5
$Me_5CpTiCl_3$	60	74.8	2.6	22.6	−91.0
$CpTiF_3$	260	81.8	1.4	16.8	−95.0
$MeCpTiF_3$	310	81.9	1.2	16.9	−92.7
Me_2CpTiF_3	605	82.0	2.0	16.0	−95.0
Me_3CpTiF_3	350	84.0	1.1	14.9	−94.1
Me_4CpTiF_3	350	80.4	1.9	17.7	−89.9
Me_5CpTiF_3	350	74.6	2.8	22.5	−87.9

[a] kg BR/mol Ti h.

2.2. Polymerizations

A 1 l glass autoclave was charged successively with toluene, MAO and 1,3-butadiene, isoprene or 1,3-pentadiene. The polymerization was started by addition of the metal compound solution. The product was washed overnight with HCl solution in ethanol and stabilizer. The organic phase was neutralized and slowly added to 300 ml ethanol, where the polybutadiene precipitated. The polymer was filtered and dried under vacuum at room temperature.

Using $[Me_2Si(N^tBu)Me_4Cp)]TiCl_2$/MAO, the following polymerization conditions were used. Toluene: 200 ml, 1,3-butadiene: 10 g (0.92 mol/l), MAO: 103–1490 mg (1.78×10^{-3}–2.57×10^{-2} mol), Al/Ti ratio = 70–2800, polymerization temperature: 60 °C, titanium complex: 2.5×10^{-5} mol, polymerization time: 3 h.

2.3. Analytical methods

Viscosimetry was carried out with an Ubbelohde capillary 53001/*a* ($K = 0.005\ mm^2\ s^{-2}$) at 30 °C using toluene as solvent (polybutadiene). Molecular weight distributions were determined by gel permeation chromatography in a Waters 150-C instrument (trichlorobenzene,

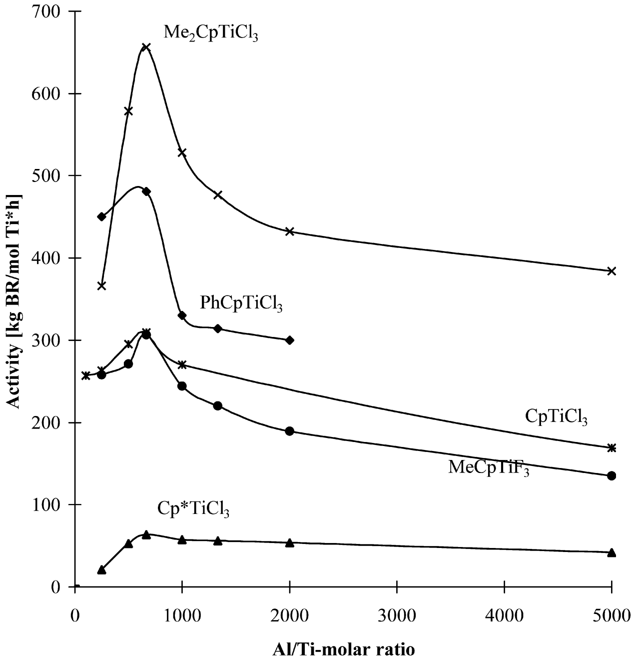

Fig. 3. Dependence of the activity of the polymerization of 1,3-butadiene on the Al/Ti molar ratio and different half-sandwich titanium complexes. Polymerization conditions: 100 ml toluene, 10 g 1,3-butadiene, 0.29 g MAO, polymerization temperature = 30 °C, polymerization time = 20 min.

135 °C). The Mark-Houwink constants have been reported in the literature [15]. Differential scanning calorimetry analyses were performed on a Mettler Toledo DSC 821e. ^{13}C NMR spectra were collected on a Bruker-MSL 300 instrument using polymer solutions in $CDCl_3$ at 50 °C (polybutadiene).

3. Results and discussion

3.1. Polybutadiene

Using R_nCpTiX_3 (X = Cl, F)/MAO catalysts for the butadiene polymerization, the dependence of the activity on the Al/Ti molar ratio was studied. The ratio was varied from Al/Ti = 200 up to 5000 (Fig. 3). All catalysts show a maximum of the activity by an Al/Ti ratio of 700. The activity decreases then with higher ratios and by longer reaction times [9]. Opposite to the styrene polymerization, the optimum of the fluorinated compound is not shifted to a lower Al/Ti ratio than for the chlorinated catalysts.

Opposite to the cyclopentadienyl titanium trihalogenides, the activities for the constrained geometry catalyst (CGC) $[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2$/MAO (Fig. 2) show no maximum (Fig. 4) but much lower values. With an increasing Al/Ti molar ratio, the activity is increasing.

This effect is found for different polymerization temperatures. The molecular weight of the obtained polybutadiene is independent of the Al/Ti ratio.

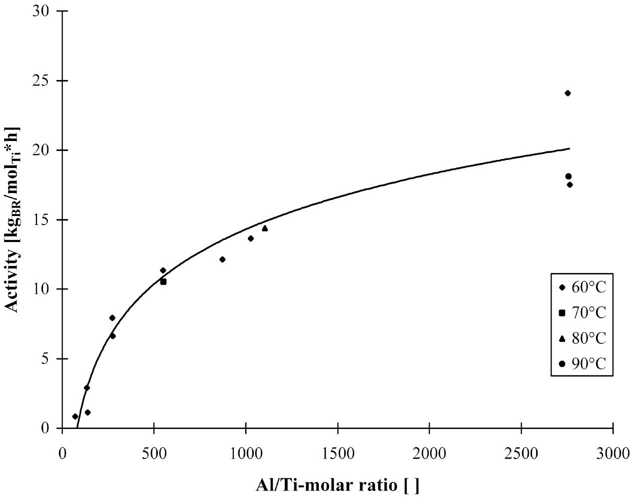

Fig. 4. Activities of the 1,3-butadiene polymerization by $[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2$/MAO catalyst in dependence of the polymerization temperature.

There is a large influence for the CGC catalyst of the molecular weight on the polymerization temperature (Fig. 5). The molecular weight decreases from 1 300 000 by 60 °C to 550 000 by 90 °C. It is remarkable that there is no large change in the microstructure if the CGC or the $CpTiCl_3$ catalyst is used (Table 2). The 1,4-*cis* part is 75–78%, the 1,4-*trans* 0–3%, the vinyl part 19–22%. By high polymerization temperatures, the *cis*-1,4 part increases slightly and the 1,4-*trans* part decreases. As of a higher vinyl part, the glass transition temperatures are higher (− 83 °C) than those measured for polybutadienes obtained by $RCpTiX_3$ catalysts (− 95 °C, Table 1).

3.2. Polyisoprene

Half-sandwich titanium compounds can also polymerize isoprene. The activities are much lower than for the polymerization of 1,3-butadiene. The catalysts used and polymerization conditions are illustrated in Table 3.

As of steric effects, the unsubstituted cyclopentadienyl compound is more active than the substituted ones. For isoprene the fluorinated compounds are much more active

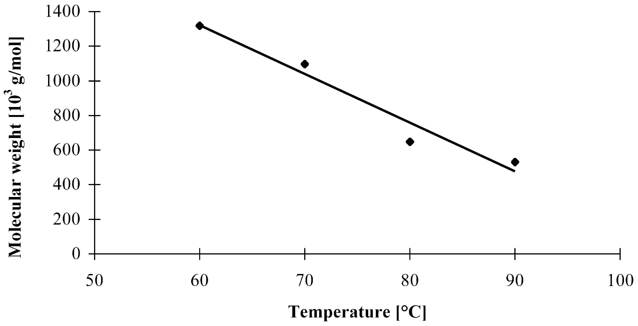

Fig. 5. Polymerization of 1,3-butadiene by $[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2$/MAO catalyst. Influence of the polymerization temperature on the molecular weight of the obtained polymer.

Table 2
Microstructures of polybutadienes obtained by the polymerization of 1,3-butadiene at different polymerization temperatures and Al/Ti molar ratios. Catalyst: $[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2/MAO$

Polymerization temperature (°C)	Al/Ti molar ratio	1,4-*cis* (%)	1,4-*trans* (%)	1,2 (%)	T_g (°C)
60	270	75.1	2.8	21.7	− 83.4
60	1030	75.3	2.4	22.0	− 84.6
60	2750	77.1	2.9	19.6	− 81.5
70	550	74.2	3.1	22.3	− 82.0
80	1100	76.5	1.1	22.4	− 82.4
90	2760	78.0	< 0.5	22.0	− 82.4

(up to a factor of 30) than the chlorinated ones. The glass transition temperature of the polyisoprenes is about − 52 °C. The microstructure is similar to that of the polybutadienes.

It is possible to synthesize copolymers of 1,3-butadiene and isoprene by using a $MeCpTiF_3/MAO$ catalyst. The copolymer has a glass transition temperature of − 60 °C.

3.3. Polypentadiene

In comparison to 1,3-butadiene, it is difficult to polymerize 1,3-pentadiene by metallocene catalysts because of the steric hindrance of the methyl group, similar to isoprene. As described in the literature, only small amounts of polypentadiene were obtained using a $CpTiCl_3/MAO$ catalyst [16]. This polymer shows a microstructure with 56.3% 1,4-*cis* and 43.7% 1,4-*trans* units [17]. Therefore, we carried out a screening to look for a more active catalyst. The 1,3-pentadiene was dried 3 days over triisobutyl aluminium and then distilled. The content of $(Z)-(E)$-isomers was determined by gas chromatography to be 22% *Z*- and 78% *E*-1,3-pentadiene.

Table 3
Homopolymerization of isoprene. Polymerization conditions: 50 ml toluene, 50 ml isoprene. $[Ti] = 5 \times 10^{-5}$ mol/l, Al/Ti = 200, $T_p = 30$ °C, $t_p = 5-24$ h

Catalyst	Activity (g IR/mol Ti h)	T_g (°C)
$CpTiCl_3$	28	− 52.0
$Me_5CpTiCl_3$	8	n.d.
$CpTiF_3$	840	− 50.3
$MeCpTiF_3$	250	− 51.2
Me_5CpTiF_3	29	n.d.

n.d., not detected.

Table 4
Polymerization of 1,3-pentadiene by different metallocene/MAO catalysts, polymerization temperature = 30 °C, 30 mg MAO, 25 ml 1,3-pentadiene, 25 ml toluene, $10^{-6}-10^{-4}$ mol metallocene, polymerization time = 5–24 h

Catalyst	Activity (kg polymer/mol cat h)
Cp_2ZrCl_2	5.0
$CpTiCl_3$	9.7
$Me_5CpTiCl_3$	9.1
$CpTiF_3$	9.5
$[Me_2C(Cp)(Flu)]ZrCl_2$	6.7
$[En(Ind)_2]ZrCl_2$	6.9
$[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2$	7.3
$[Me_2Si(N^tBu)(Me_4Cp)]VCl_2$	36.5

Table 4 gives an overview on the polymerization activity of 1,3-pentadiene by different metallocene and half-sandwich catalysts.

Nearly all catalysts used show only a polymerization activity between 5 and 9.7 kg of polypentadiene/mol of catalyst in 1 h. Only the activity for the CGC catalyst based on a vanadium metal is remarkably high in comparison to the other catalysts and reaches a value of 36.5 kg polym./mol V h. This vanadium complex was optimized with regards to achieve higher activities. Fig. 6 shows the activities at different temperatures in a glass autoclave.

The maximum of the activity with 172 kg polym./mol V h was observed at a polymerization temperature of 50 °C. The polymerization activity also depends on the concentration of 1,3-pentadiene in the starting phase. If the concentration was increased from 4 to 10 mol/l, the activity increased by the factor of 2.4.

The viscosity average molecular weight was measured to be nearly independent of the polymerization temperature and varies between 90 000 and 110 000. The glass transition temperature of these polypentadienes is 42 °C.

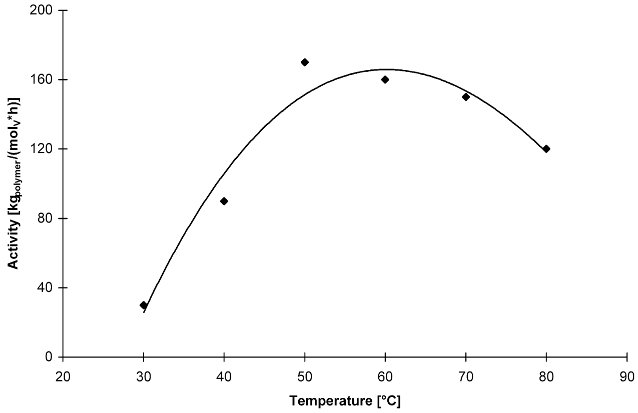

Fig. 6. Temperature dependency of the polymerization of 1,3-pentadiene with $[Me_2Si(N^tBu)(Me_4Cp)]VCl_2/MAO$. Polymerization conditions: $c(cat) = 2 \times 10^{-4}$ mol/l, $c(monomer) = 4$ mol/l, Al/V molar ratio = 300.

4. Conclusions

For the polymerization of 1,3-butadiene with R_nCpTiX_3/MAO catalysts, the highest activities can be achieved using the catalysts containing two methylsubstituents on the cyclopentadienylring. High molecular weights over 1 million can be obtained.

Due to sterical reasons, the unsubstituted $CpTiX_3$/MAO catalysts are more active in the polymerization of isoprene and 1,3-pentadiene. In the case of isoprene, the fluorinated catalyst is much more active than the chlorinated one, but for 1,3-pentadiene both substituents yield nearly the same low activity.

The CGC catalyst is able to polymerize all three monomers, but only for 1,3-pentadiene the activities are significantly higher compared to R_nCpTiX_3/MAO catalysts.

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