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New Elastomers by Metallocene Catalysis

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SUMMARY: Elastomers with new microstructures such as ethene propene diene terpolymers (EPDM), polybutadiene (PB) and polyisoprene, can be synthesized by metallocene or other single site catalysts. EPDM elastomers show a narrow molecular weight distribution, low transition metal concentration and mainly 1,2-insertion of the propene units. Polybutadienes are prepared with high efficiency by different half-sandwich titanium chlorides or fluorides and methylalumoxane as cocatalyst. Di- or trimethyl substituted cyclopentadienyltitanium trihalogenides are the most active compounds with activities of about 700 kg polybutadiene/mol Ti·h. These catalysts produce polybutadiene with an interesting microstructure which consists of 80 % cis, 1 % trans and 19 % vinyl structures.

Introduction

Metallocene/MAO catalysts are very efficient tools in producing not only polyolefins but also elastomers such as ethene/1-olefin copolymers (PO), EPDM, PB, and polyisoprene with a narrow molecular weight distribution[1-3)]. The polymerizations can be carried out in solution or in the gas phase[4)].

The copolymers of ethene and propene, with a molar ratio of 1:0,5 up to 1:2, are of great industrial interest. These EP-polymers show elastic properties and, together with 2-5 wt% of dienes as third monomers, they can be vulcanised by sulfur. Since there are no double bonds in the backbone of the polymer, it is less sensitive to oxidation reactions. Ethylidenenorbornene (ENB), 1,4-hexadiene and dicyclopentadiene are used as dienes. In most technical processes for the production of EP and EPDM rubber, soluble or highly disposed vanadium components have been used in the past. Similar elastomers, which are less coloured, can be obtained with metallocene/MAO catalyst at a much higher activity[5)]. The regiospecificity of the metallocene catalysts towards propene leads exclusively to the formation of head-to-tail enchainments. Ethylidenenorbornene polymerises via vinyl polymerisation of the cyclic double bond and the tendency of branching is low. The molecular weight distribution of about 2 is narrow[6)]. In the past the molecular weight (MW) of metallocene EPDM was low. New catalysts open up the possibility to increase the MW.

High branching which is caused by the incorporation of long chain olefins into the growing polymer chain is obtained with silyl bridged amidocyclopentadienyltitanium compounds, the

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constrained geometry catalysts (CGC)[7,8]. They are useful for the production of thermoplastic polyolefins (TPO) which find applications in interior and exterior automotive applications and increased rapidly over the past years. TPOs are replacing traditional engineering thermoplastics and thermosets in automotive parts such as bumper fascia, claddings, air dams and instrument panels. The replacement is due mainly to the performance properties, formulation flexibility and low cost offered by TPOs.

Amorphous EPDM and high molecular weight semi-crystalline EPR have been widely used as impact modifiers for TPOs. Dow has a polyolefin elastomer with the name ENGAGE already on the market[9].

ENGAGE polyolefin elastomer has been introduced recently as an impact modifier for toughening polypropene. The low-temperature dart impact test results show that the low density elastomer has achieved toughening efficiency similar to EPDM and high molecular weight EPR. At comparable molecular weight and density, this polyolefin elastomers have very good low-temperature Izod impact properties.

Some metallocene-based systems are also active for 1,3-diene polymerisation. Although the polymerisation mechanism of dienes is different from that of monoalkenes, metallocene catalysts have proved to be of interest also for the polymerisation of this class of monomers. They have permitted new polymers to be obtained, some of which are highly stereoregular, and have provided an opportunity to gain a deeper insight into the mechanism of polymerisation[10]. The greatest industrial interest is given for the production of polybutadiene. Polybutadiene belongs to the most important rubber for technical purposes. In 1999, more than 2 million tons were produced worldwide, that is about 20 % of all synthetic rubbers[11]. One part is produced by using different types of Ziegler catalysts with titanium, nickel, cobalt or neodymium as transition metal and shows a high content up to 98 % of 1,4-cis linked diene units. The other part is catalysed by lithium butyl showing a different microstructure of about 40 % cis-1,4, 49 % trans-1,4 and 11 % vinyl (1,2) linked units. The vinyl structures are useful for subsequent vulcanisation by sulfur. It is difficult to produce polybutadienes with microstructures having a high content of vinyl but low content of trans-1,4 structures.

Porri und Olivera[12,13] demonstrated that the half sandwich complex biscyclopentadienyl titanium trichloride ($CpTiCl_3$) in combination with methylaluminoxane (MAO) is able to polymerise 1,3-butadiene to a rubber which contains high cis-1,4 and 1,2-structure contents but a low percentage of trans 1,4-microstructure. An explanation for the differences between the mechanism of polymerisation of butadiene and olefins is given by Porri. The first 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 the diene polymerization and a σ-type bond in the olefin polymerisation. The other difference is the control of the insertion and the coordination of the monomer to the transition metal. We have reported[14,15] that substituted half sandwich complexes of titanium – especially if they are fluorinated – are more active for the polymerization of styrene than unsubstituted and corresponding chlorinated compounds. There is a similarity between the polymerization behaviour of styrene and butadiene[16].

EPDM Elastomers

New metallocene catalysts were used to synthesize EPDM elastomers[17]. C_s and C_1-symmetric zirconocenes show high activities and are able to incorporate ENB. A pentalene-bridged zirconocene (Fig. 1) resulted in polymers with high molecular weights at high incorporations of propene.

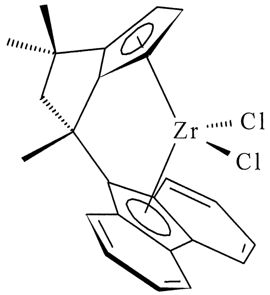

Figure 1: Structure of the pentalen-bridged zirconocene $[Me_3Pen(Flu)]ZrCl_2$.

The experiments were carried out in a 1 liter Büchi autoclave equipped with an additional internal cooling system. Monomer feed of the gaseous monomers was maintained with a press-flow controller. For the standard experiment, the reactor was evacuated at 95°C and charged subsequently with 500 ml toluene, MAO and the required amount of ENB. Ethene (E) and propene (P) were added afterwards, so that the total monomer concentration was 1 mol/l. Polymerization was started by addition of the toluenic metallocene solution. During the reaction, the total pressure was kept constant by supplying ethene. Polymerization was quenched by injection of 5 ml of ethanol.

Table 1 shows the results of the polymerization by 30 °C.

Table 1. Activities and incorporation of monomers of the preparation of EPDM by metallocene/MAO catalysts. $X_E/X_P/X_{ENB}$ = 0,3/0,6/0,1 (mol/l).

Catalyst	Activity (kg Pol/mol Zr·h)	Molecular weight M_η	Composition of the polymer (wt %) E	P	ENB
$[Me_2C(Cp)(Flu)]ZrCl_2$	6 600	12 000	50	40	10
$[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2$	13 000	19 000	56	36	8
$[Me_2C(3\text{-}^{tert}\text{-}BuCp)(Flu)]ZrCl_2$	16 000	48 000	66	28	6
$[Me_2C(3\text{-}PhCp)(Flu)]ZrCl_2$	59 000	16 000	54	40	6
$[Ph_2C(Cp)(Flu)]ZrCl_2$	21 000	49 000	51	41	8
$[Me_3Pen(Flu)]ZrCl_2$	1 600	72 000	38	53	9
$[Me_2Si(Cp)(Flu)]ZrCl_2$	123 000	121 000	56	33	11
$[Me_2Si(Cp)_2]ZrCl_2$	37 000	3 000	23	52	25

Metallocene-Polybutadiene

The half sandwich complexes of titanium, synthesized and used for the polymerization of 1,3-butadiene are shown in Fig. 2[18).

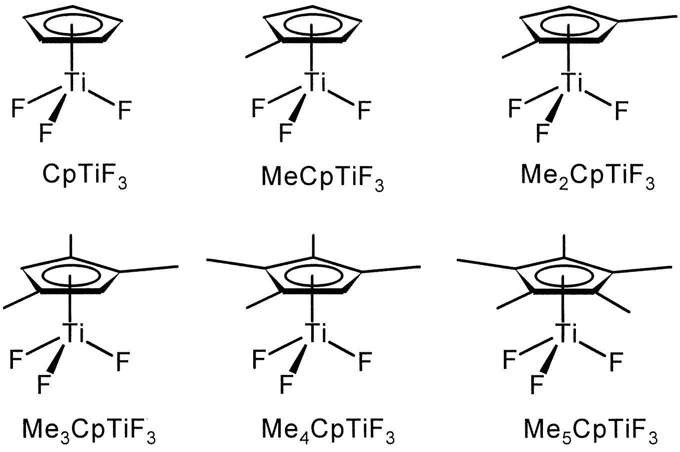

Figure 2: Different substituted cyclopentadienyl titanium trifluorides used for the polymerization of butadiene.

The polymerizations were carried out in a glass reactor filled with 100 ml of toluene, 10 g of 1,3-butadiene and 290 mg of MAO. The concentration of the titanium complex was $5 \cdot 10^{-5}$ mol/l resulting in an Al/Ti-ratio of 1000. The polymerizations were carried out at 30 °C for 20 minutes. The results are shown in Table 2.

Table 2. Activities of titanium fluoride/MAO catalysts for the polymerisation of 1,3-butadiene in 100 ml toluene and molecular weights of the obtained polybutadienes. 10 g 1,3-butadiene, 0,29 g MAO, [Ti] = $5 \cdot 10^{-5}$ mol/l, Al/Ti = 1000, T = 30 °C, polymerization time = 20 min.

Catalyst	Activity*	Molecular weight
$CpTiF_3$	260	970 000
$MeCpTiF_3$	310	1 220 000
Me_2CpTiF_3	605	1 280 000
Me_3CpTiF_3	350	1 250 000
Me_4CpTiF_3	350	1 500 000
Me_5CpTiF_3	350	1 400 000

*Activity : kg BR/mol Ti·h

The activities of the 1,3-dimethylcyclopentadienyl titaniumtrifluorides are the highest and reach about 700 kg BR/mol Ti·h. Chlorinated complexes show nearly the same activity[18)].

Only the highly substituted fluorinated compounds (Me_4CpTiF_3, Me_5CpTiF_3) are by the factor of two more active than the corresponding chlorinated ones. The activity reaches a maximum of all catalysts after a short induction period of 5 to 10 minutes. After this the activity decreases to a certain value for each catalyst that stays constant for a longer period of time up to one hour.

The substitution pattern influences the induction period. The most active compounds show the shortest induction period, whereas the less active ones need a clearly longer period. The kinetic orders of the butadiene concentration and the catalyst concentration are one. At constant Al:Ti ratio the polymerisation rate is given by

$$r_p = k_p \cdot c_{cat} \cdot c_\beta$$

where c_β is the concentration of butadiene. Even at low Al:Ti ratios of 200 the activities are quite high (Fig. 3). The activity increases with an increasing Al:Ti ratio, reaches a maximum by Al:Ti = 500-700 and decrease then with higher Al:Ti ratios. A similar picture was found for the fluorinated complexes.

Surprisingly, high molecular masses are obtained for the polybutadienes produced with these new catalysts (Tab. 2). The molecular masses increase by increasing the substitution of the cyclopentadienyl ligand.

Most important for an industrial application are the microstructures and the glass transition temperatures. The glass transition temperatures range from –87,9 to –95,0°C (Table 3). The polybutadienes produced with the most methyl substituted ligand have the highest content of vinyl units and the lowest glass transistion temperature.

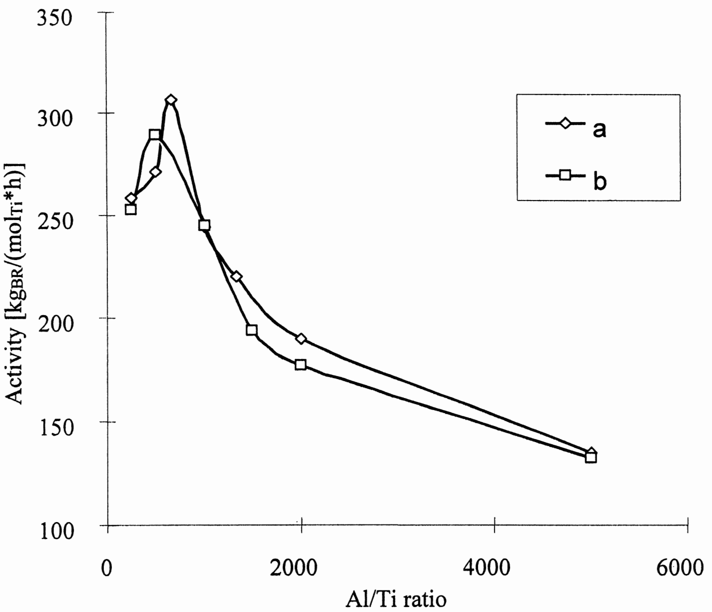

Figure 3: Activities of the polymerisation of 1,3-butadiene in dependence of the Al:Ti molar ratio using $CpTiCl_3$/MAO in 100 ml toluene by 30 °C. Butadiene: 10 g, tp = 20 min, a = constant MAO concentration of 0,29 g; b = constant Ti concentration of $5 \cdot 10^{-6}$ mol/l.

Table 3. Microstructure and glass transition temperatures of the polybutadienes produced by fluorinated catalysts.

Catalyst	1,4-cis [%]	1,4-trans [%]	vinyl [%]	T_g [%]
$CpTiF_3$	81,8	1,4	16,8	- 95,0
$MeCpTiF_3$	81,9	1,2	16,9	- 92,7
Me_2CpTiF_3	82,0	2,0	16,0	- 95,0
Me_3CpTiF_3	84,0	1,1	14,9	- 94,1
Me_4CpTiF_3	80,4	1,9	17,7	- 89,9
Me_5CpTiF_3	74,6	2,8	22,5	- 87,9

For all catalysts, the 1,4-cis structure units of the polybutadiene range between 74,6 and 84%, the 1,4-trans between 1,1 and 2,8%, and the 1,2(vinyl) units between 14,9 and 22,5%. There is also no influence of the Al:Ti ratio of the catalyst on the obtained microstructure of the polybutadiene (Tab. 4).

Table 4. Influence of the Al:Ti ratio on the microstructure, glass transition temperature and molecular weight using the catalyst $MeCpTiF_3$; 0,29 g MAO, T = 30 °C.

Al:Ti mol ratio	1,4-cis [%]	1,4-trans [%]	vinyl [%]	Tg [°C]	Mw [g/mol]
500	79,4	2,9	17,7	- 92,0	1 050 000
1 000	81,9	1,2	16,9	- 92,7	1 220 000
2 000	81,8	0,9	17,3	- 92,3	1 010 000
10 000	79,9	2,9	17,2	- 92,3	880 000

The chemo- and stereospecifity is not changed. Only the molecular weight decreases with very high Al:Ti ratios. The microstructure of the polybutadienes change if the temperature is changed (Tab. 5).

Table 5. Influence of the polymerization temperature on the microstructure of the obtained polybutadiene using the catalyst $MeCpTiF_2$, 0,29 g MAO, Al:Ti = 5000.

Polymerization temperature [°C]	1,4-cis [%]	1,4-trans [%]	vinyl [%]	Tg [°C]
0	83,6	2,4	14,0	- 94,1
30	80,3	1,9	17,8	- 92,3
60	78,8	3,1	18,1	- 91,8
90	72,5	7,4	20,1	- 90,2

The 1,4-cis content decreases with increasing of the polymerization temperature while the 1,4-trans and the vinyl content increase. Because of the increasing 1,2-insertion, the glass transition temperatures are decreasing. The differences between the anti- and synstructure elements of the transition state complexes become smaller.

Similar microstructures are obtained when using the chlorinated complexes or $CpTiCl_3$ supported on MAO treated silica[19)]. By polymerising with the supported catalyst in a gas phase reactor, the activity increases to 14 500 kg BR/mol Ti·h, with a molecular weight of 1,900,000 g/mol. Activity further increases when $CpTiCl_3$ catalyst is prealkylated with small quantities of triisobutylaluminium. It could be suggested that a Ti(III)-species is responsible for the polymerization.

Instead of MAO also perfluoro phenylborate as cocatalyst for the polymerzation of 1,3-butadiene can be used. This cocatalyst is very sensitive to impurities. Therefore small amounts of triisobutyl aluminium (TIBA) are added to the feed, which works as scavenger. Another function of TIBA is the alkylation of the titanium compound. The following results are obtained (Tab. 6).

Table 6. Polymerization of 1,3-butadiene by $Me_5TiCl_3/Ph_3C[B(C_6F_5)_4]/TIBA$ at 30 °C.

Me_5TiCl_3 concentration	$5\cdot10^{-5}$ mol/l
$Ph_3C[B(C_6F_5)_4]$ concentration	$5\cdot10^{-5}$ mol/l
TIBA/Ti ratio	1000
Polymerization time	90 min
Activity	28 kg PB/mol Ti·h
Molecular weight	480 000
Microstructure	73% 1,4-cis, 2,5% 1,4-trans, 24,5% vinyl
Glass transition temperature	- 90,9°C

Compared with MAO as cocatalyst, the borate produces a polybutadiene with a lower activity and molecular weight. The vinyl content is the highest found with half sandwich titanocenes.

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