Ethene-Butadiene Copolymers by Single-Site Catalysts

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Summary: Constrained geometry catalysts ($[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2$) were used to copolymerize ethene and 1,3-butadiene. It is possible to incorporate 17 mol% of butadiene, other catalyst systems such as $CpTiCl_3$/MAO show much lower incorporation. More than 300 000 kg of copolymer can be obtained by one mol of the catalysts in one hour. The microstructure of the copolymers has been investigated by ^1H- and ^{13}C-NMR spectroscopy. The butadiene is incorporated mainly in 1,4-trans- and 1,2-structure. The high amount of 9-29 % of vinyl groups offers the possibility of an easy vulcanisation. The molecular weights of these elastomers are high with values of 250 000. Important is the low glass transition temperature of –28 °C of a copolymer with 7 mol% of butadiene.

Keywords: catalysts; copolymerization

Introduction

Metallocenes and other single-site catalysts are highly active for the production of precisely designed polyolefins and copolymers [1-5]. Especially zirconocene methylalumoxane (MAO) catalysts, half-sandwich amido titanium complexes in combination with perfluorophenylborate have opened a frontier in the area of new copolymer synthesis and processing. The copolymers obtained show different microstructures, tacticities, and properties.

1,3-Butadiene can be polymerised by half-sandwich complexes substituted cyclopentadienyltitanium halogenides in combination with MAO to a rubber which contains high 1,4-cis-and 1,2-structures but low 1,4-trans-microstructures [6,7].

It was shown that fluorinated half-sandwich titanocenes are more stable towards temperatures as chlorinated ones and also useful for the production of polybutadiene with a high amount of 1,2-structures [8]. Similar results are obtained by constrained geometry catalysts. Table 1 shows results of the microstructures and glass transition temperatures of polybutadienes obtained by using a $[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2$/MAO catalyst by different polymerisation temperatures and Al/Ti molar ratios. The content of 1,4-cis-structures is more than 75 %, that of 1,2(vinyl)structures more than 19 %, and that of 1,4-trans 3% and less. Single-site catalysts are important for copolymers such as ethene-1-octene, ethene-styrene and ethene-1,3-

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butadiene. These polymers show increased impact strength and toughness, better melt characteristics, or elasticity, and improved clarity in films.

Table 1. Microstructures of polybutadienes obtained by the polymerisation of 1,3-butadiene by different polymerisation temperatures and Al/Ti molar ratios;
Catalyst: $[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2$/MAO, $2{,}5\cdot10^{-5}$ mol in 200 ml toluene.

Polym.Temp. (°C)	Al/Ti-molar ratio	1,4-cis (%)	1,4-trans (%)	1,2 (%)	Tg (°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

Result and Discussion

The CGC catalyst $[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2$/MAO was used to prepare ethene/1,3-butadiene copolymers because it is able to homopolymerize as well ethene as 1,3-butadiene (see Table 1). The experiments were carried out discontinually in a 1 L glass autoclave (for polymerization conditions see Table 2). The conversion was only 2 % to have constant conditions during the polymerisation. Fig. 1 shows the activity of the copolymerisation of ethene and butadiene in dependence of the molar ratio of butadiene in the feed.

Table 2. Polymerization conditions for the ethene-1,3-butadiene copolymerization.

solvent	200ml toluene
polymerization temperature	60°C
polymerization time	10 - 60 min
butadiene	0,4 - 14 g
MAO	400 mg
CGC	$9\cdot10^{-8}$ - $3\cdot10^{-7}$ mol

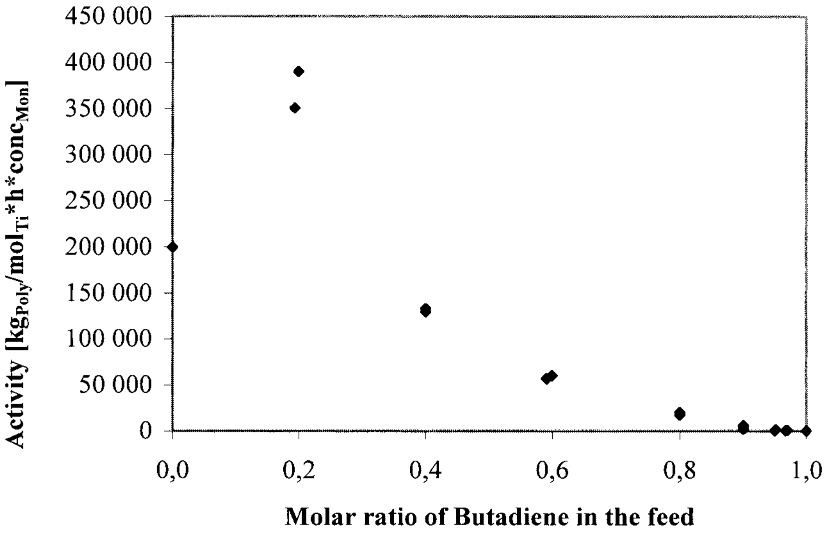

Figure 1. Activities of the copolymerization of ethene and 1,3-butadiene in dependance of the molar ratio of butadiene X_B in the feed. Catalyst: $[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2/MAO$.

The activity increases with small ratios of butadiene and reaches a maximum at 390 kg copolymer/mol Ti · h · [monomer] and decreaseb then continually with higher molar ratios of butadiene. A similar tendency is presented by the molecular weights of the obtained polymers which are about 300 000 up to 50 mol% of butadiene in the feed to decrease to 60 000 by 90 mol%.

Melting and Glass Transition Temperatures

It has been proven by ^{13}C-NMR spectroscopy and GPC-analysis that the obtained Polymer is a monomodal copolymer. In addition to that, the melting temperature of the copolymer (Fig. 2) decreases continually from 115 °C by 20 mol% of butadiene in the feed to only 20 °C by 80 mol%. Therefore we are sure that we have obtained a pure copolymer and no mixtures of homo- and copolymers.

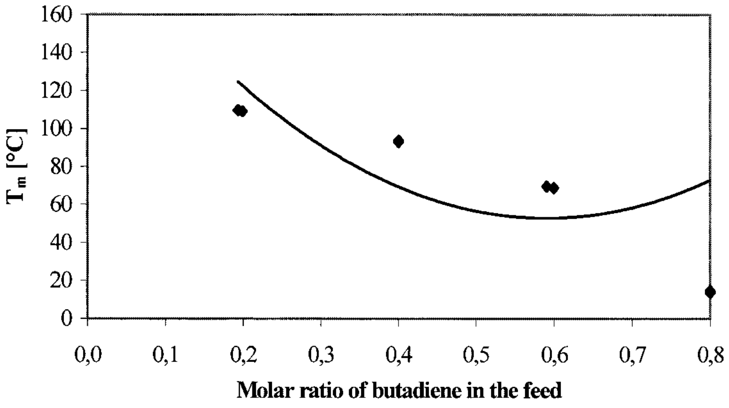

Figure 2. Melting points of ethene-butadiene copolymers in dependence of the molar ratio of butadiene in the feed.

The picture is different for the glass transition temperatures (Fig. 3). These show a minimum by 80 mol% of butadiene in the feed of –28 °C and increase with higher butadiene concentrations. Above a molar ratio of 0,8 for butadiene, the copolymers are amorphic.

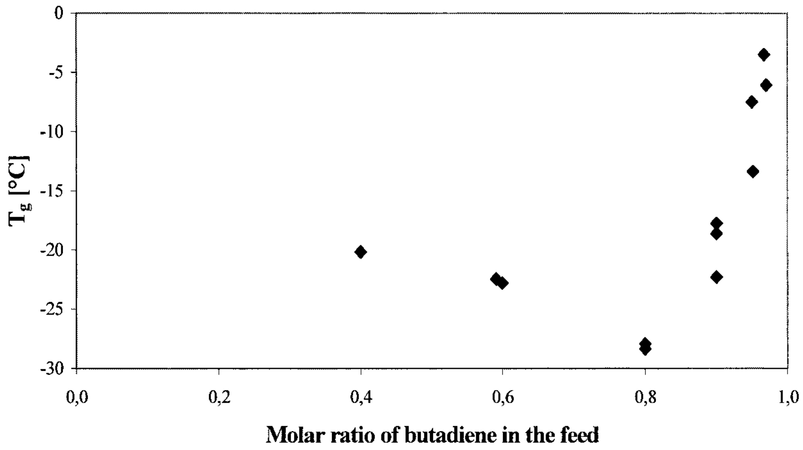

Figure 3. Glass transition temperatures of ethene-butadiene copolymers in dependence of the molar ratio of butadiene in the feed.

Microstructures

The microstructure of the ethene/1,3-butadiene copolymers were investigated by ^{13}C-NMR and ^{1}H-NMR measurements. The ^{1}H-NMR signals for the 1,2-insertion could be detected without problems. Fig. 4 shows the part of 1,2-insertion of the total butadiene insertions in relation to the mol% of butadiene in the copolymer.

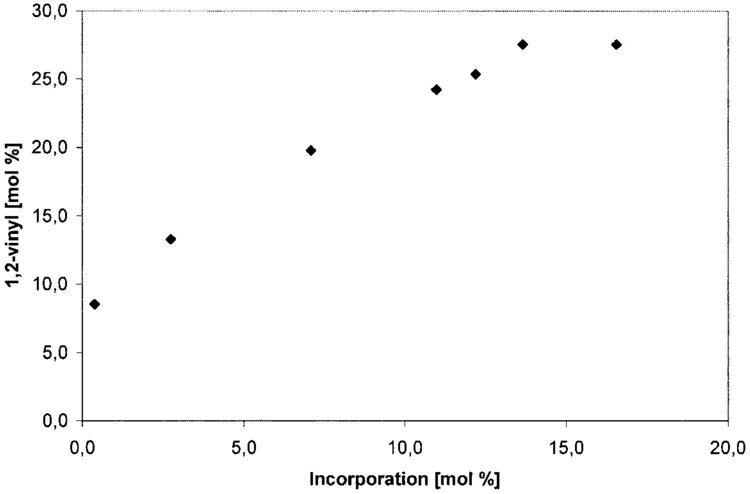

Figure 4. 1,2-vinyl part of butadiene units in the ethene-butadiene copolymers in relation to the total inserted butadiene.

The part of 1,2-insertion increases with higher amount of butadiene in the copolymer and reaches over 25 mol%. More difficult was the detection of the cis- and trans-part by ^{13}C-NMR measurements. Surprisingly, no cis-microstructures could be detected. All signals seen were those for 1,4-trans microstructures. Compared to the homopolymerization of butadiene by the same CGC catalysts (see Tab. 1), where the polybutadiene show mainly 1,4-cis and 1,2-microstructures, this picture is changed for the copolymerisation. If butadiene is incorporated in an ethene-polymer chain, it is incorporated mainly in 1,4-trans- and in small parts in 1,2-microstructures but not in 1,4-cis units. Similar results were obtained by the copolymerisation of ethene and butadiene by classical metallocene catalysts (Cp_2ZrCl_2) 9) which incorporates butadiene much slower than the CGC catalyst.

There is a change in the polymerisation mechanism from the homopolymerization of butadiene to the copolymerisation of ethene/butadiene. In the copolymer no blocks of butadiene can be observed. Therefore the maximum of butadiene concentration in an ethene butadiene copolymer could be 50 mol% with an alternating microstructure. It is difficult to reach such high concentration of butadiene (Fig. 5).

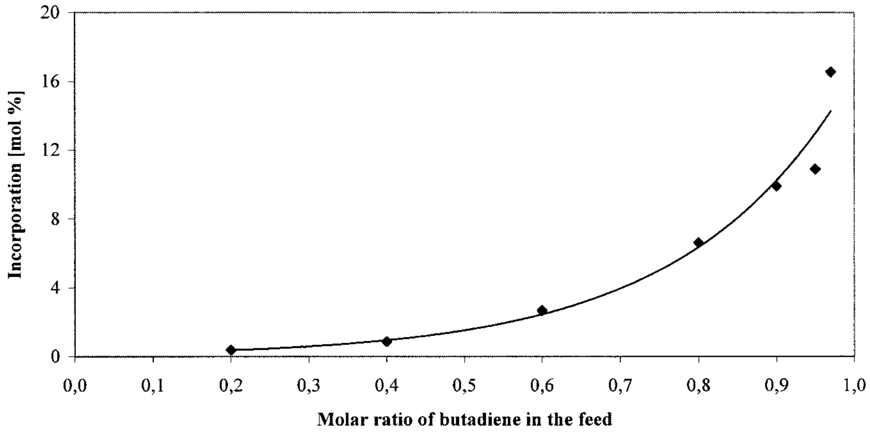

Figure 5. Butadiene incorporation in mol% in a ethene-butadiene copolymer in dependence of the molar ratio of butadiene in the feed.

By a molar ratio of butadiene in the feed of 0,2 only 0,5 mol% of butadiene is incorporated. This value increased to 16 mol% by a molar ratio of 0,96 butadiene in the feed.

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