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Copolymerisation Properties of Siloxy-Substituted bis(Indenyl)zirconocene Catalysts: Modified Rheological Behaviour

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SUMMARY: The combination of the copolymerisation ability and vinyl end group selectivity of siloxy substitution of ethylene-bridged bis(indenyl) zirconium dichlorides suggest these catalyst as potential ones for the production of polyethylene containing small amounts of long chain branching. The role of the polymerisation conditions with these highly active catalysts can clearly be seen. Furthermore low contents of multiple branches may occur, even though the probability of attaching several macromonomers into one chain is low. The effect on melt rheological behaviour depends on both the amount of long chain branching and the length of the branch. Moreover the position of the siloxy group is very important. Polymers synthesized with catalysts, where the siloxy group is in position 1, give peculiar rheological behaviour resembling cross-linked networks although the polymers are completely soluble.

Introduction

In spite of the excellent polymerisation properties of metallocene catalysts in general, in terms of product homogeneity and mechanical properties, there still remains a severe problem of processability due to the usually narrow molar mass distributions, which are reflected in the viscosity behaviour of the produced polymers. As a consequence, high-density polyethylene (PE-HD) still stays outside several large application areas, e.g. paper coating.

From low-density polyethylene technology (PE-LD) the importance of long chain branching (LCB) is well known to modify the melt viscosity behaviour, such as viscosity vs. shear rate, neck in, melt elasticity etc. It is also known that the branches needed for polyethylene are at least 270 C-atoms long, longer than the entanglement chain length, to cause changes in melt rheological behaviour. As a result, branches resulting from the incorporation of long α-olefins are not long enough to be effective in this respect, which is in agreement with our studies on branches in the range of C_{10} -

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C_{20}. On the other hand, very low concentrations of branches are effective for rheological modifications, already 1 branch per 10 000 carbon atoms is estimated to be enough. In PE-LD the concentration is in the range of 1 branch per 1000 carbons.

It is claimed that Dow's constrained geometry catalyst (CGC) produces polymer chains having narrow molar mass distribution but with high levels of long chain branching to improve processability. Other suitable catalyst types appear, according to our results on LCB formation, to be bis-indenyl zirconocene catalysts and their modified versions. We have previously reported a new class of ethylene –bridged siloxy substituted metallocenes, which are highly active in ethylene polymerisations and reveal optimum polymerisation behaviour at low Al/Zr ratios.1) The objective of this study was to examine the influence of the siloxy substituents and their position on the rheological behaviour in ethylene polymerisations.

Experimental Part

Chemicals: The metallocene catalysts *rac*-ethylenebis(1-(*tert-butyldimethylsiloxy*)-indenyl)zirconium dichloride (Cat **1**), *rac*-ethylenebis(2-(*tert*-butyldimethylsiloxy)-indenyl)zirconium dichloride (Cat **2**), and *rac*-ethylenebis(1-(tri-isopropylsiloxy)-indenyl)zirconium dichloride (Cat **3**) were prepared according to literature procedures.2) In addition, the *meso* forms of Cat **1**, *meso*-**1**, and of Cat **2**, *meso*-**2** were included. Ethylene (AGA, grade 3.5), pentane and comonomer 1-hexene (Aldrich, 99%) were purified by passage through a series of columns containing molecular sieves (not for 1-hexene), CuO, and Al_2O_3. Toluene (Merck, GR grade) was refluxed over Na/benzophenone and subsequently distilled under nitrogen. Methylaluminoxane (MAO) (10%w/w in toluene) and *rac*-ethylenebis(1-indenyl)-zirconium dichloride (**EBIZ**) were purchased from Witco.

Polymerisation and Characterisation: All polymerisations were carried out in a 0.5 dm^3 stainless steel autoclave according to literature procedures.3) The overall reaction rates and polymer yields were kept low to avoid mass and heat transfer problems.

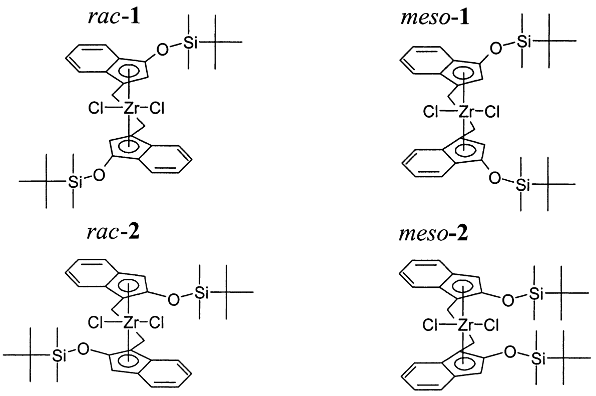
Molar masses and molar mass distributions were determined using a Waters 150C high-temperature size exclusive chromatograph (SEC) equipped with a RI detector. Branching was studied with a Waters 150cvplus SEC-OLV instrument equipped with both RI and on-line viscosity detectors. Comonomer content was determined by FTIR (Nicolet Magna 750) analysis calibrated with ^{13}C NMR (Varian Gemini 2000 300-

MHz). Double bonds in the polymers were analysed by ^{1}H NMR spectroscopy or FTIR. The linear viscoelastic behaviour of the polymer melts was studied with a Rheometric Scientific SR-500 rotational rheometer. Measurements were performed under nitrogen blanket; measurements details and stability checks have been reported earlier.4) For the uniaxial melt elongation studies, a modified type5) of the uniaxial elongational rheometer of Münstedt 6) was used.

Results and Discussion

Prerequisites for *in situ* LCB are the formation of vinyl chain ends and ability to incorporate them into a growing chain. Vinyl-terminations occur if chain transfer to monomer, β-hydrogen elimination or δ-bond metathesis takes place. However, isomerization related to β-H elimination or chain transfer to monomer can give undesired *trans*-vinylene groups. Vinylidene groups are produced through chain transfer to comonomer after 1,2-insertion, while *trans*-vinylene structures are produced through chain transfer to comonomer after 2,1-insertions, and saturated end groups through chain transfer to aluminium or hydrogen.7)

LCB formation thus requires from the catalyst first, termination mechanisms giving vinyl terminated chains and secondly, good copolymerisation ability to incorporate them into a growing polymer chain. Based on our earlier results on copolymerisation with the catalyst $Et(Ind)_2ZrCl_2$ (**EBIZ**)4), we have investigated the copolymerisation behaviour of modified bis-indenyl catalysts. We have found that interesting homo- and copolymerisation properties are received by modifying the bis-indenyl catalysts with siloxy substituents in 1 or 2 position. These catalysts show improved total activities at normally used Al/Zr ratios and moreover substantially increased activities with very low Al/Zr-ratios compared to unsubstituted bisindenyl zirconocenes.8,10) Influence of the position of the siloxy substituent and the hydrogenation of the ligand on copolymerisation ability is analysed in ethylene-co-1-hexene copolymers from the reactivity ratios demonstrated in Figure 1. The siloxy substitution at the 1-position of the indenyl ligand improves considerably the copolymerisation ability ($r_E = 16$), whereas the siloxy substitution at the 2-position appears to slightly reduce the copolymerisation ability ($r_E = 36$), as is the case also with the hydrogenation of the siloxy substituted catalysts, compared to the normal **EBIZ**.10) We have seen on the other hand, if the substituent is a silyl group in 1-position, the copolymerisation ability is quite poor.



rac-**1** *meso*-**1** *rac*-**2** *meso*-**2**

rac-**1** r_E 16 ± 1
$r_{1\text{-}H}$ 0.005

meso-**1** r_E 10 ± 1
$r_{1\text{-}H}$ $<<0.01$

rac-**2** r_E 36 ± 3
$r_{1\text{-}H}$ < 0.01

meso-**2** r_E 11 ± 1
$r_{1\text{-}H}$ <0.01

Fig. 1: Comonomer response of siloxy substituted *bis*-indenylzirconocenes.

The 2-siloxy substituted bis-indenyl catalysts appear to have excellent vinyl end group selectivity, especially at low ethylene pressures, revealed in Figure 2. They are far more vinyl end group selective than their 1-siloxy substituted counterparts, which indicates that siloxy substitution in 2-position suppresses the isomerization reaction and thus *trans*-vinylene formation in chain transfer reactions.[11]

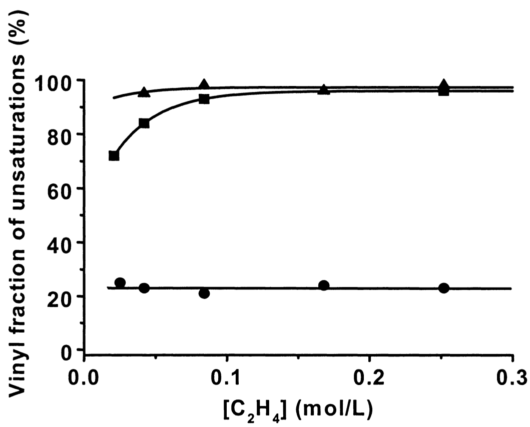


Fig. 2: The influence of siloxy substitution and ligand hydrogenation on vinyl end group selectivity in ethylene homopolymerisation at 80 °C, where the symbols ▲ is Cat **2**, ■ is **EBIZ** and ● is the hydrogenated **EBIZ.**

Another interesting feature of the siloxy substituted bis-indenyl catalysts is the fact that their diastereomers show dissimilar polymerisation properties. The *racemic* forms produce the highest molar masses in ethylene polymerisation, whereas the *meso* forms are somewhat better copolymerisation catalysts in ethylene-α-olefin copolymerisation. We have also found that chain transfer to monomer is the predominant termination mechanism. The *meso* diastereomers undergo chain transfer after 1,2-insertion of comonomer, which can be seen as the absence of *trans*-vinylene structures. All of the diastereomers produced rheologically modified polymers. 11,12)

The response of the rheological behaviour to the copolymerisation ability and vinyl end group selectivity of these catalysts was studied from their dynamic modulus curves. The frequency dependence of the dynamic modulus of the polymers produced with the 1-siloxy substituted EBIZ catalyst, which was very active in copolymerisation and showed greatly increased total activity in copolymerisation, is demonstrated in Figure 3. The copolymer indicates a network–like behaviour, although the polymer was completely soluble and obviously not cross-linked, whereas the homopolymer behaves as a typical linear polymer, judged on the basis of flow activation energy (E_a) of 27 kJ/mol. Apparently there is a certain effect of mass transfer limitation improving the competitive state of macromonomer insertion. Furthermore the copolymer exhibited a higher molar mass than the corresponding homopolymer.

In the case of the polyethylene produced with the 2-siloxy substituted catalyst the contribution of the elastic modulus G' seems to be large in comparison with that of the viscous modulus G'' and a clearly modified LCB type of rheological behaviour is seen as revealed in Figure 4. The measured complex viscosities (η^*) are clearly elevated in comparison to the measured molar masses, as the theoretical zero shear rate viscosity η_0 of linear polyethylene at 190°C should follow the equation proposed by Raju et al.14): $\eta_0 = 3{,}4 \cdot 10^{-15} \cdot M_w^{-3.6}$. Furthermore E_a values are at the level of 48-57 kJ/mol, which values resemble those of PE-LD. At lower polymerisation pressures broader rheological polydispersity is seen judged from higher η^* values and earlier crossover points of storage and loss modulus curves with frequency, although, measured by SEC, the molar mass distribution remains narrow and the polymer P25 exhibits the same molar masse (Mw = 110000) as polymer P21, polymerised at higher pressure, (Figure 4).

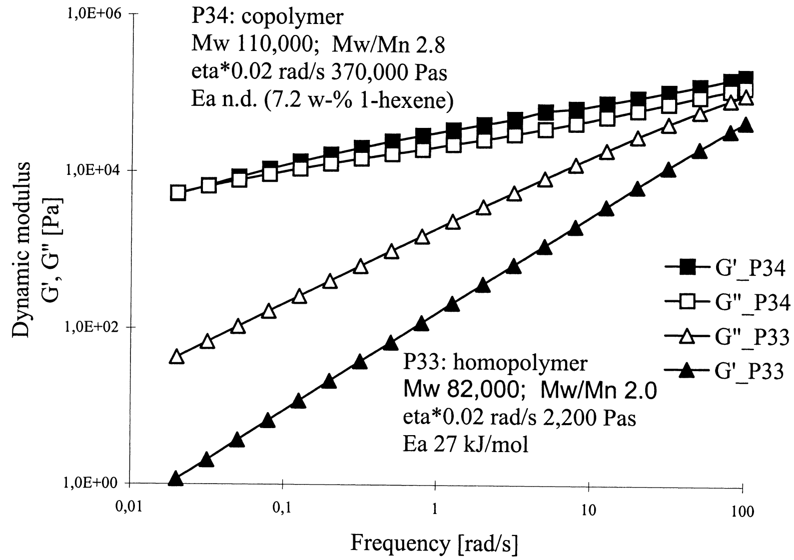


Fig. 3: Dynamic storage modulus G' and loss modulus G" as a function of oscillation frequency at 190 °C for Cat **1** ethylene homopolymer P33 and ethylene/hexene copolymer P34 at 80°C in pentane.

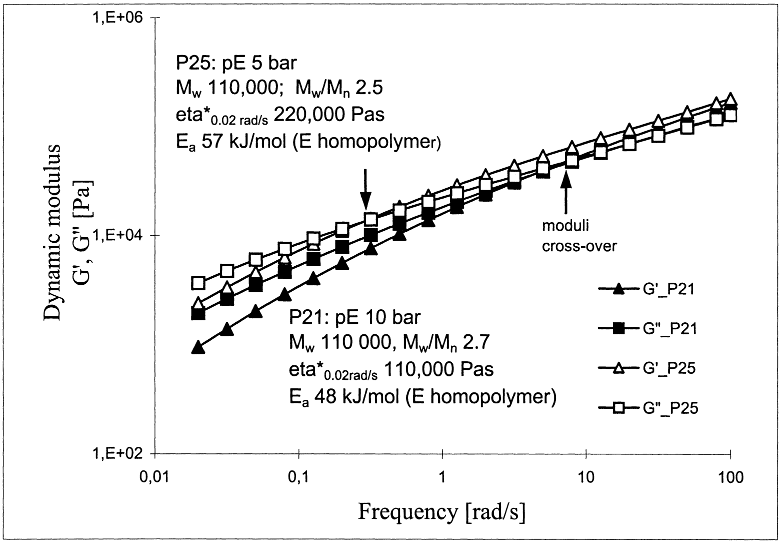


Fig. 4: Dynamic storage modulus G' and loss modulus G" as a function of oscillation frequency at 190 °C for Cat **2** in ethylene homopolymerisation at 80°C in pentane at two different ethylene pressures.

In Figure 5 the dynamic modulus as function of frequency is demonstrated for a catalyst with fairly large siloxy groups in position 1. This catalyst is the most active one, both in homo- and copolymerisation. The polymers produced with this catalyst exhibit in addition to the large elastic response throughout the frequency range, also a peculiar curvature, which again indicates a network-like rheological behaviour both in homo- and copolymerisation in spite of, that even in this case, the polymers are totally soluble and were thermally stable during the measurements.

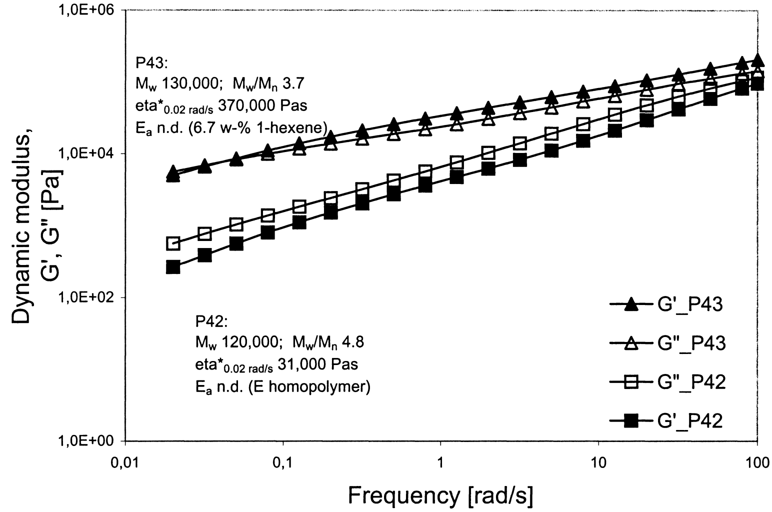


Fig. 5: Dynamic storage modulus G' and loss modulus G" as a function of oscillation frequency at 190 °C for Cat **3** ethylene homopolymer P 42 and ethylene/hexene copolymer P 43 at 80°C in pentane.

Direct evidence of LCB is fairly difficult to get due to the low concentrations of the branches. For this reason indirect rheological evidence of branches is gained through melt rheological measurements.[13] However, the rheological changes, we can see in Figures 3-5, suggest that there are different topological structures in the chain branching. We can differentiate star, comb and multiple branched structures revealed in Figure 6. Though probability of multiple branched structures is low, its presence is indicated through melt uniaxial elongational measurements with constant strain rate, which clearly show strain hardening effect for polymers polymerised by using 1-siloxy substituted catalysts.[15]

- **Star**
- broaden relaxation spectrum
- increase E_a

- **Comb**
- broaden relaxation spectrum
- increase in E_a depending on arm length

- **Multiple branched**
- broaden relaxation spectrum
- increase E_a
- strain hardening in elongation

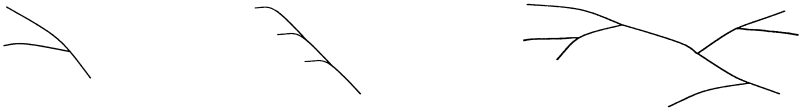


Fig. 6: Different possible long chain branching structures and their effect on the melt rheological behaviour.

Conclusions

The excellent copolymerisation properties of siloxy substituted bis-indenyl zirconocene catalysts, as well as, their vinyl end group selectivity can be applied to produce new functional properties in polyolefins. One of the most important functional properties is modified rheology.

Long chain branching in polyethylene produced with metallocenes depends highly on the catalyst and polymerisation conditions. Particularly the vinyl end group selectivity and the copolymerisation ability are among the most important features of the catalyst. The vinyl end group selectivity is also dependent on the ethylene concentration. Selectivity becomes purer when the ethylene concentration is decreased. The amount of LCB can be controlled by monomer, comonomer and hydrogen concentration. Mass transfer limitation is of significance when highly active siloxy substituted catalysts are used. Differences in rheological behaviour suggest that both amount and distribution, i.e. topology, of the LCB varies with the catalyst structure and polymerisation conditions. Vinyl end group selectivity and comonomer response correlate well with observed LCB of polyethylene synthesized with zirconocenes.

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