Structure and Properties of Ethene Copolymers Synthesized by Metallocene Catalysts

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STRUCTURE AND PROPERTIES OF ETHENE COPOLYMERS SYNTHESIZED BY METALLOCENE CATALYSTS

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ABSTRACT

The microstructure of ethylene copolymers based on 1-hexene, 1-octene, and norbornene as comonomers was studied and related to its melting, crystallization, and glass transition behavior as well as to tensile strength.

INTRODUCTION

With metallocene catalysts it is possible to synthesize ethene copolymers with narrow molecular weight distribution and homogeneous chemical composition. Crystallinity, melting temperature, and density of the PE are reduced by the comonomer incorporation. With increasing comonomer content linear low density polyethene and highly flexible copolymers (polyolefin elastomers) are obtained. Correlations between catalyst and copolymerization behavior are widely described in the literature, while influences on morphology, mechanical, and rheological properties of mLLDPEs are studied very little. Although the homogeneity of the copolymers

has an extremely positive effect on their profile of use, it is supposed to complicate the processing.

The aim of our investigation is to study the correlations between the micro-structure of the copolymers, the morphology, and the thermal and mechanical properties.

EXPERIMENTAL

Synthesis

Ethene was copolymerized with 1-hexene, 1-octene, and norbornene. The copolymers were synthesized with a comonomer content ranging from 0 to about 12 mol%.
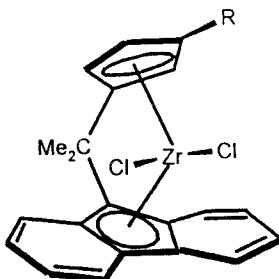
(1) R = 3-tert. butyl   (2) R = methyl

$[Me_2C(3\text{-}tBuCp)(Flu)]ZrCl_2$ (1), in combination with methylaluminoxane (mao) as a cocatalyst, was used for the copolymerizations with 1-hexene, 1-octene, and norbornene. Additionally, ethene-norbornene copolymerization by $[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2$ (2)/mao was performed. In our investigations of the thermal and mechanical properties, we integrated three commercial ethene-octene copolymers: AFFINITY and the ENGAGE types EG 8150 and EG 8200 (all made by Dow Chemical Co.).

Sample Preparation

Sheets of 100 x 100 x 1 mm in dimension, were made by compression molding: the polymer sample was pressed between two foils of aluminum at 180°C with low pressure for 5 minutes, with 20 bar for 5 minutes, and with 50 bar for 1 minute. The samples were cooled with 15 K/min. to 50°C and cut to a

specimen, dimensions 80 x8 x 1 mm, for determination of mechanical properties or 50 x 8 x1 mm for d.m.a.

Methods

Differential Scanning Calorimetry (d.s.c.)

A Perkin Elmer DSC-7 calorimeter was employed. Samples were subjected to a cycle of first heating, cooling, and second heating with a scan rate of 10 K/min. over a temperature range from -10°C to +150°C.

It is necessary to analyze the first heat to compare the d.s.c. crystallinity with those determined by WAXS and density at room temperature. The amount of crystallites already melting by $T < 0°C$ increases with increasing comonomer content. The crystallinity at room temperature α_{DSC} (25°C) is partly up to 15% lower than the maximal accessible crystallinity (at -50°C). The crystallinity α_{DSC} (25°C) was estimated by partial integration.

$$\alpha_{DSC} (25°C) = \Delta H_{part. (25°C - T\ end)} / \Delta H_0$$

ΔH_0 (heat of fusion of a 100% crystalline PE) = 293 J g^{-1}

Dynamic Mechanical Analysis (d.m.a.)

Samples of the dimensions 50 x 10 x 2 mm were analyzed using an Explexor 150N instrument (GABO Qualimeter) in the temperature range between -120 and +100°C. The heating rate was 2 K/min. and the frequency 10 Hz.

Wide Angle X-ray Scattering (WAXS)

WAXS investigations were performed by using Cu Kα radiation with the X-ray diffractometer HZG 4/A-2 (Seifert-FPM GmbH) equipped with an energy-dispersive detector EDR 288 (RönTec GmbH). Transmission measurements were carried out in a scattering range $2\Theta = 5 ... 50°$ supposing $\Delta 2\Theta = 0.1°$ and t = 10 s.

The X-ray crystallinity was determined by a simple reflection area method inside the scattering range $2\Theta = 11 ... 31°$ (symmetric amorphous halo with a maximum at about 19.5° for polyethylene and about 18.5° for polynorbornene, respectively, were assumed).

Determination of Mechanical Properties

Samples of dimensions 80 x 8 x 1 mm were tested using a Zwick 1456 universal testing machine. Tensile strength and elongation at break were determined with a deformation rate of 20 mm/min. and a clamping distance of 45 mm.

RESULTS AND DISCUSSION

Microstructure

Ethene-norbornene copolymers produced by (1) were shown to feature a micro-structure containing only odd numbered ethene sequence lengths. This special microstructure is the result of a chain migratory insertion and the steric hindrance by the tBu-group (thus, there is only ethene insertion on site B).
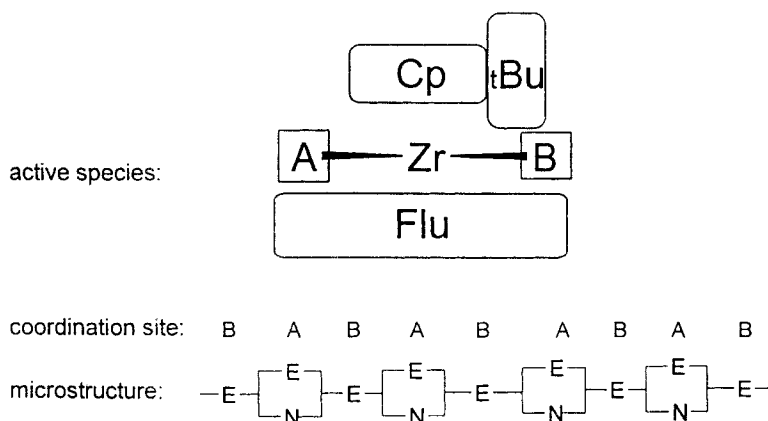
Ethene-norbornene produced by (2), as well as the ethene-1-hexene and the ethene-1-octene copolymers produced by (1), show a statistical distribution (1st order markovian statistics) of odd and even numbered ethene sequence lengths [1]. In these cases, it is proposed that insertion occurs only from site B and the growing chain stays on site A.

Crystallinity

Crystallinities of the compression molded samples were determined at room temperature by WAXS, d.s.c., and density (Figure 1). The values of all three methods are in good agreement.

The crystallinity is affected by the number of branched chains (content of the comonomer unit) and their shape (linear or cyclic). With increasing content on hexene or octene the crystallinity decreases. The influence of the linear comonomers on the crystallinity is as strong as that of the cyclic comonomer. With norbornene as
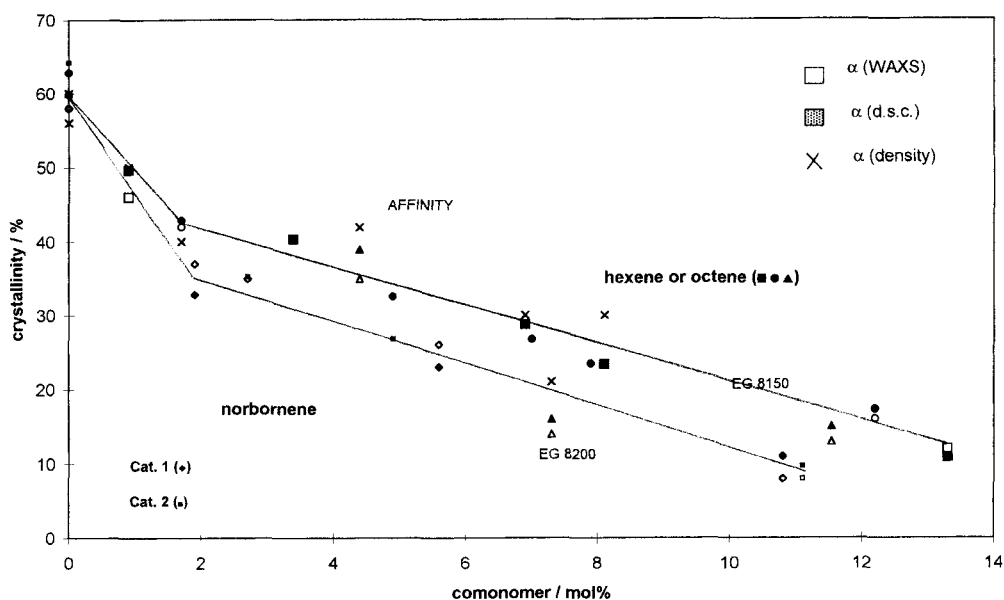
Figure 1.   Crystallinity vs. chemical structure of the comonomer and comonomer content (compression molded samples, 1st heat).

comonomer, the crystal morphology of the LLDPE samples is more disturbed than with hexene or octene. The different catalysts used for the ethene-norbornene copolymerization show no distinct consequences for the crystallinity.

Dynamic Mechanical Properties

The variation of the comonomer content strongly influences the α and β relaxation of ethene-octene and ethene-norbornene copolymers (Figure 2).

Decreasing glass transition temperatures (β relaxation) of ethene-octene and ethene-hexene copolymers with increasing comonomer content are associated with a higher content of more flexible segments and a decrease of crystallinity. The drop of crystallinity is reflected in a shift of the α relaxation to lower temperatures (partial overlapping of α and β relaxation) and a lower α intensity. Beside the decreasing crystallinity, Bensason *et al.* [2] priority attributed this tendency to a poorer crystal surface order.

With decreasing crystallinity, the storage modulus strongly drops above the glass transition.

Figure 2.   Loss factor tan δ of ethene-octene and ethene-norbornene copoly-mers.
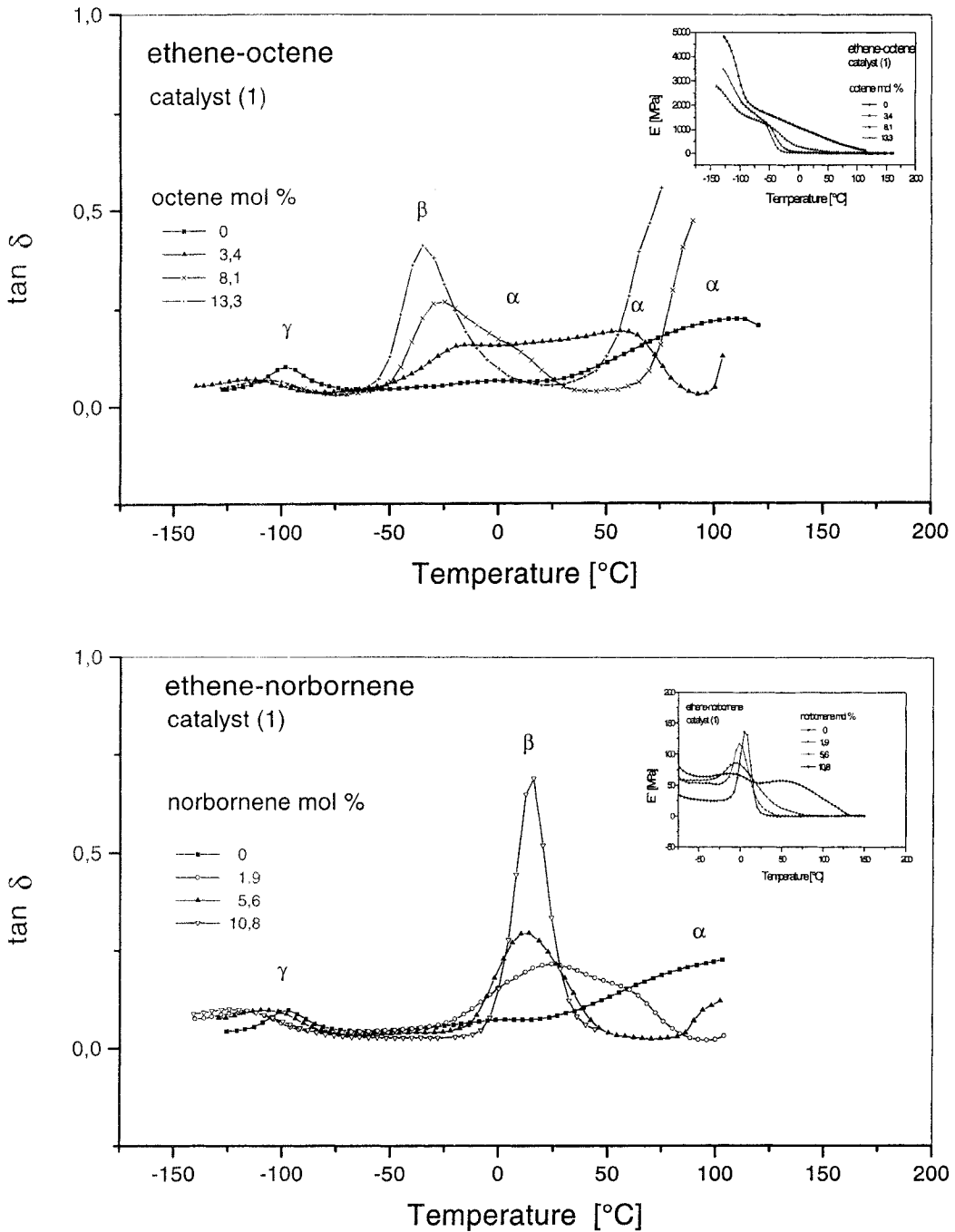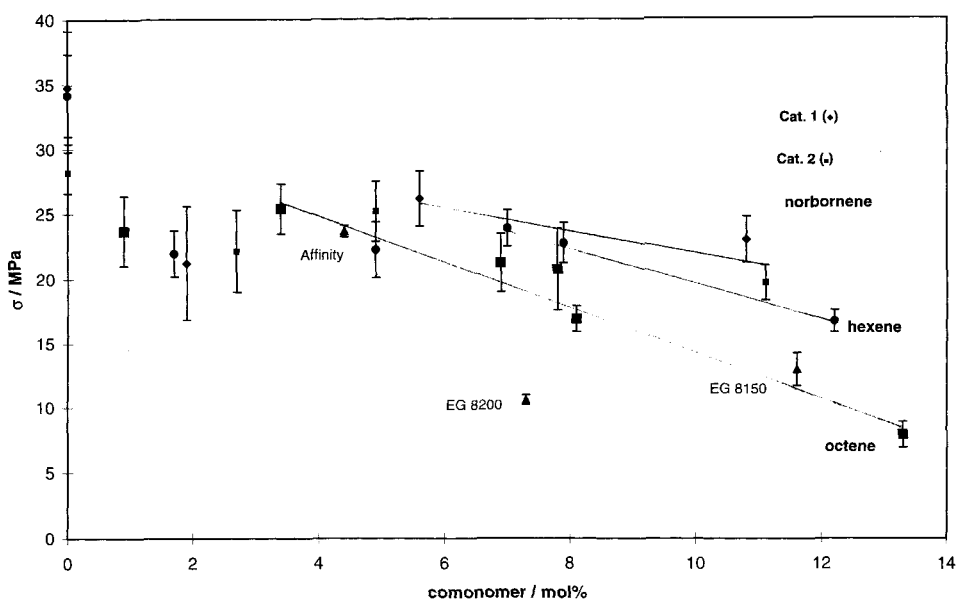
Figure 3.   Tensile strength of ethene-hexene, ethene-octene and ethene-norbornene copolymers.

In contrast to the ethene-octene copolymers, the glass transition temperatures of the ethene-norbornene copolymers slightly increase with higher comonomer content in spite of decreasing crystallinity due to a growing incorporation of rigid norbornene chain segments (competition situation).

Tensile Strength

The introduction of comonomers results in a decrease of the tensile strength compared to the homopolymers (Figure 3). This result is independent of the chemical structure and the catalysts used and especially pronounced at low comonomer concentrations. At more than 10 mol% comonomer content, the norbornene copolymers still exhibit acceptable strength, while the strength of octene copolymers is decreased.

CONCLUSION

The effect of the different comonomers on the properties depends on their chemical structure. The incorporation of aliphatic comonomers reduces the crystal-

linity resulting in reduced tensile strength. Beside the fact that the incorporation of the alicyclic norbornene results in a stronger decrease in crystallinity compared to the linear comonomers, the tensile strength is much less reduced.

Different catalysts used for the ethene-norbornene copolymerization caused different microstructures. However, the expected variations in mechanical and thermal properties could not be proved.

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