Ethene−Norbornene Copolymerization with Homogeneous Metallocene and Half-Sandwich Catalysts: Kinetics and Relationships between Catalyst Structure and Polymer Structure. 4. Development of Molecular Weights

Dieter Ruchatz and Gerhard Fink*

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1,
45470 Mülheim an der Ruhr, Germany

Received July 15, 1997; Revised Manuscript Received April 22, 1998

ABSTRACT: The molecular weights of ethene−norbornene copolymers, produced with various metallocene− and amidocyclopentadienyl−methylaluminoxane (MAO) catalysts, have been determined by high-temperature gel-permeation chromatography: with one exception, increasing molecular weights were found with an increasing norbornene content in the copolymer. This observation is due to the fact that the β-hydride elimination process is not possible in the case of norbornene, because of special steric conditions of the cis-2,3-exo inserted norbornene; other possible termination reactions are discussed, considering the specialties of the norbornene. The effect of the catalyst structure on the molecular weights is discussed in terms of steric and electronic factors of the different ligands: sterically less hindered ligands produce ethene−norbornene copolymers with relatively low molecular weights; ligands with a larger extension and electron-pushing effect such as the fluorenyl ligand, induced the formation of high molecular weights. Additional alkyl groups at the indenyl or fluorenyl ligand increased the molecular weights additionally.

Introduction

In the first two papers of this series we presented the results of the kinetic measurements and of the ^{13}C NMR spectroscopic investigation of the ethene−norbornene copolymers;[1,2] the third paper dealt with the determination of the copolymerization parameters and the copolymerization diagrams.[3] In the present and fourth paper, we demonstrate the dependence of the molecular weights on the catalysts used and the norbornene content in the copolymers and discuss the reasons for finding these results.

The height of the molecular weight determines the technical suitability of the ethene−norbornene copolymers, because important material properties such as tensile strength and breaking tension are influenced by the molecular weight. The lower limits for a technical use lies around 10^5 g mol^{-1}. Besides a high activity, the catalyst must produce ethene−norbornene copolymers with large enough molecular weights. For this reason, the molecular weights of the produced copolymers were determined by high-temperature gel-permeation chromatography (GPC). In this connection we want to describe briefly the problems arising with the determination of the molecular weights of copolymers: Conventional GPC works without any viscosity detection, which means that the molecular weights are not directly accessible, because the calibration of the GPC is mostly based on narrow polystyrene standards in conjunction with the universal calibration of Benoit.[4,5] In this case, the proper molecular weights of the polymers measured can only be calculated if the Mark−Houwink constants are known. Especially in the case of the ethene−cycloolefin copolymers this happens to be untrue; the molecular weights of these copolymers that have been published in the literature[6−9] are compulsorily referring to polyethene. This situation can be improved by coupling a GPC with a viscosity detector. In addition to a concentration detector, the intrinsic viscosity $[\eta]$ can be measured online, and with the help of the universal calibration, the molecular weights can be calculated more precisely.

Experimental Section

Polymer Characterization. The molecular weights were determined on a high-temperature GPC, equipped with a viscosity detector (H 502 B, Viscotek) and an evaporative mass detector (PL-EMD 950, Polymer Laboratories). The measurements were carried out in Decaline at 150 °C; 4-*tert*-butylcalix[4]arene (Aldrich, 1 g·L^{-1}) was used as an internal time marker for the flow-rate correction and 2,6-di-(*tert*-butyl)-4-methylphenol ("Ionol", Aldrich, 1 g·L^{-1}) was used as stabilizing agent and antioxidant. Three separation columns (10^6, 10^3, and 10^5 Å, SDV, Polymer Standards Service, Mainz, Germany) were used in series; universal calibration[4,5] was performed with narrow polystyrene standards (Polymer Standards Service, Mainz, Germany). The calculation of the molecular weights was performed with the Viscotek software package (version 2.7).

Results and Discussion

The following diagrams (Figures 1−3) show the development of the molecular weights of the ethene−norbornene copolymers depending on the norbornene content and the catalyst used: With the exception of the $Me_2Si[Me_4CpN^tBu]TiCl_2$ catalyst, increasing molecular weights were found with increasing norbornene content in the copolymer; the molecular weight distribution lies with values measuring between 2.0 and 2.8 in the typical range noted for metallocene and half-sandwich catalysts. Ethene−norbornene copolymers with the largest molecular weights were produced by the metallocenes of the $^iPr[(3\text{-}R{-}Cp)Flu]ZrCl_2$ type ranging between 300 000 and 2 000 000 g·mol^{-1}. The molecular weights of the copolymers, which were produced by the catalysts of the $^iPr[(3\text{-}R\text{-}Cp)Ind]ZrCl_2$ type

S0024-9297(97)01044-9 CCC: $15.00

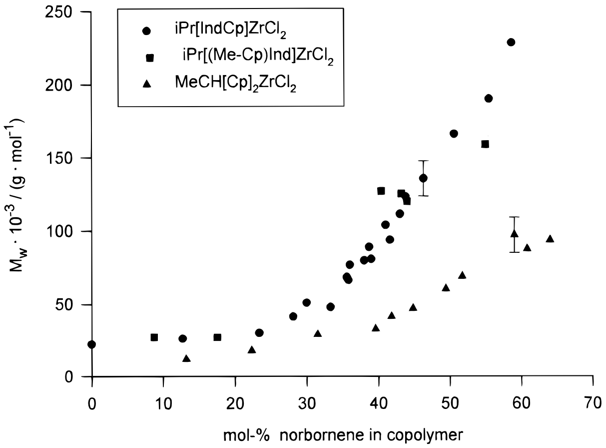

Figure 1. Molecular weights of the ethene−norbornene copolymers vs norbornene content in copolymer (cocatalyst, methylaluminoxane; solvent, toluene; polymerization temperature, 70 °C).

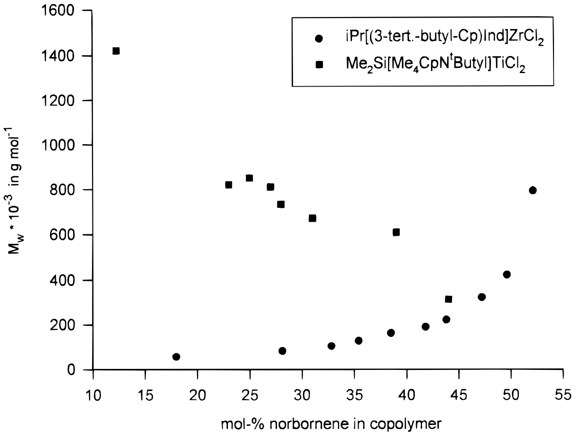

Figure 2. Molecular weights of the ethene−norbornene copolymers vs norbornene content in copolymer (cocatalyst, methylaluminoxane; solvent, toluene; polymerization temperature, 70 °C).

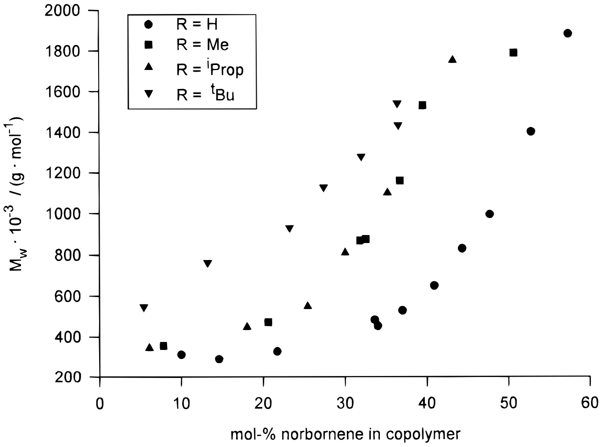

Figure 3. Molecular weights of the ethene−norbornene copolymers vs norbornene content in copolymer (catalyst, ^{i}Pr[(3-R-Cp)Flu]ZrCl$_2$ with R = H, Me, *i*-Pr, or *t*-Bu; solvent, toluene; polymerization temperature, 70 °C).

lie in the middle ranges, measuring values between 20 000 and 800 000 g·mol^{-1}. The lowest molecular weights were produced by the sterically less hindered MeCH[Cp]$_2$ZrCl$_2$ catalyst.

The molecular weights of the ethene−norbornene copolymers that were produced with the half-sandwich catalysts Me$_2$Si[Me$_4$CpN^{t}Bu]ZrCl$_2$ and Me$_2$Si[FluN^{t}Bu]ZrCl$_2$ could not be measured, because the copolymer samples showed a very low solubility. In the case of R-(+)-Me$_2$Si[Me$_4$CpNCH(CH$_3$)-1-naphthyl]TiCl$_2$, only one copolymer sample with a norbornene content of 28 mol % showed a high enough solubility and the molecular weight found here was 350 000 g·mol^{-1}. Only one copolymerization experiment was carried out with the chromium half-sandwich catalyst C$_2$H$_4$[Me$_4$CpNMe$_2$]Cr-(η^1,η^1-C$_4$H$_8$); the norbornene content was 29 mol % and the molecular weight found here was 350 000 g·mol^{-1}.

Summing up the results of the molecular weight determination, the following ranking can be stated: ^{i}Pr[(3-^{t}Bu-Cp)Flu]ZrCl$_2$ ≈ Me$_2$Si[(3-^{t}Bu-Cp)Flu]ZrCl$_2$ > ^{i}Pr[(3-Me-Cp)Flu]ZrCl$_2$ ≈ ^{i}Pr[(3-^{i}Prop-Cp)Flu]ZrCl$_2$ > ^{i}Pr[FluCp]ZrCl$_2$ > Me$_2$Si[Me$_4$CpN^{t}Bu]TiCl$_2$ ≈ ^{i}Pr[(3-^{t}Bu-Cp)Ind]ZrCl$_2$ ≈ R-(+)-Me$_2$Si[Me$_4$CpNCH(CH$_3$)-1-naphthyl]TiCl$_2$ > ^{i}Pr[IndCp]ZrCl$_2$ ≈ ^{i}Pr[(Me-Cp)Ind]ZrCl$_2$ > MeCH[Cp]$_2$ZrCl$_2$.

The molecular weight depends on the relation of chain growth to chain transfer and chain termination reactions. In the case of metallocene- and half-sandwich-catalyzed olefin polymerizations, the chain-transfer reactions are dominating; chain termination occurs only in the case of an irreversible deactivation reaction of the catalyst. The following chain-termination reactions compete with each other:

(a) β-hydride eliminination under formation of a metal hydride, (b) β-hydride eliminination under participation of the monomer = chain transfer on the monomer, and (c) vinylic C−H bond activation.[10]

Woo[10−12] found the following order: β-hydride elimination < vinylic C−H bond activation < chain transfer on the monomer. In general, the molecular weights of ethene−α-olefin copolymers decrease with increasing comonomer content, because the β-hydride elimination is facilitated after insertion of, for example, 1-hexene or 1-octene.[13] In the special case of bicyclic comonomers such as norbornene, the possible chain-transfer reactions require a more detailed discussion: (a) After norbornene insertion, the chain termination via β-hydride elimination is impossible, because the β-H atom of the norbornene is in an endo position, due to cis−exo insertion; a basic requirement for the β-hydride elimination process is the coplanarity of the metal−carbon bond and the β-H atom. Due to the endo position of the β-H atom, the typical four-center transition state cannot be formed. The second possibility, i.e., the β-hydride elimination under participation of the H-atom at the bridgehead carbon atom of the norbornene, is also impossible, because of Bredt's rule. (b) The transfer reaction to the monomer requires the coplanarity of the metal atom, C$_\alpha$, C$_\beta$, and the β-H atom, which cannot be reached if the monomer inserted last is norbornene. (c) Vinylic C−H bond activation should be possible in either case, even if norbornene is inserted last. Due to sterical effects, this process is being more hindered, if norbornene is involved instead of ethene. Thus, the vinylic C−H bond activation is the only possible transfer reaction beside the transfer reaction on the aluminum, if a norbornene molecule is involved.

Another question arises concerning the influence of the catalyst structure on the molecular weights, especially the transfer reactions. Depending on the catalyst used, the molecular weights differed by a factor of 20 maximum. The influence of the catalyst structure on the molecular weights is similarily complicated as in the case of the chain-growth reaction, due to interaction of sterical and electronic effects. A quantification is, therefore, very difficult. However, the decisive factors are known:[14] (a) Steric effects: the β-hydride elimination requires a four-center transition state, in which the C_β-H σ-orbital overlaps with the empty orbital of the transition metal atom; to do this, the growing polymer chain has to first rotate around the $C_\alpha{-}C_\beta$ axis. Steric effects can increase the energy of the transition state, due to nonbonding interactions between the polymer chain and the ligand. This is also true in the case of the chain transfer reaction on the monomer. Brintzinger introduced a concept for the estimation of sterical interactions with the ligand.[15,16] In general, steric interaction increases with rising lateral extension of the ligand: Cp < Ind < Flu. In the case of the transition metals, the following order can be established, due to their differences in the atomic radius: Hf $\approx$ Zr < Ti. (b) Electronic effects: electron-pushing ligands lower the tendency for transfer reactions from a thermodynamical point of view. The electron pushing effect increases in the order Cp < Ind < Flu. Due to their different metal–carbon bonding energy, the transition metals suppress the transfer reaction in the following order: Ti < Zr < Hf.

On the basis of these sterical and electronical effects, the development of the molecular weights becomes more comprehensible: with increasing norbornene concentration the extent of the transfer reactions decrease. As a result, the molecular weight increases with increasing norbornene content. The effect of the ligand is the sum of the interaction of steric and electronic effects: The catalysts with a fluorenyl ligand produces the largest molecular weights, because the steric and electronic effects act in the same manner.

In general, additional substituents at the Cp ring suppress transfer reactions due to increased transition-state energies, which are the outcome of the greater nonbonding interactions. An example for this is the catalyst ${}^{i}Pr[(3\text{-}{}^{t}Bu\text{-}Cp)Ind]ZrCl_2$: The additional *tert*-butyl-group at the Cp ring increases the molecular weights drastically in comparison to ${}^{i}Pr[CpInd]ZrCl_2$. The sterically less hindered metallocene catalyst $MeCH[Cp]_2ZrCl_2$ produces ethene–norbornene copolymers with the lowest molecular weights, because the steric and electronic properties of this catalyst effect only a minor suppression of the transfer reactions, due to the reasons discussed above.

In contrast to this, the behavior of the half-sandwich catalyst $Me_2Si[Me_4CpN{}^{t}Bu]TiCl_2$ comes as a surprise: An increasing norbornene content decreases the molecular weight of the ethene–norbornene copolymers; on the other hand, increasing molecular weights were found with an increasing hexene content as in the case of the ethene–hexene copolymerization with this type of half-sandwich catalyst.[17] Obviously the extent of transfer reactions is dependent on the nature of the monomer, which is inserted before an ethene molecule. Possibly the norbornene unit, which is inserted before an ethene molecule, supports the transfer reactions after an ethene insertion. For a more detailed description of this phenomenon, additional experiments including those with other half-sandwich catalysts have still to be performed.

The effect of different aluminum alkyls on the ethene–norbornene copolymerization process, catalyzed by ${}^{i}Pr[CpInd]ZrCl_2$, has also been studied: besides a marked lowering of the catalytic activity, the molecular weights of the resulting ethene–norbornene copolymers decreased dramatically. A more detailed discussion of the effect of aluminum alkyls will be given in a forthcoming paper.[18]

References and Notes

(1) Ruchatz, D.; Fink, G. *Macromolecules* **1998**, *31*, 4669–4673 (first of four paprs in this issue).
(2) Ruchatz, D.; Fink, G. *Macromolecules* **1998**, *31*, 4674–4680 (second of four paprs in this issue).
(3) Ruchatz, D.; Fink, G. *Macromolecules* **1998**, *31*, 4681–4683 (third of four paprs in this issue).
(4) Benoit, H.; Crubisic, Z.; Rempp, P.; Decker, D. *J. Chem. Phys.* **1966,** *63*, 1507.
(5) Crubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Part B: Polym. Lett.* **1967,** *5*, 753.
(6) Kaminsky, W.; Noll, A. *Polym. Bull.* **1993,** *31*, 175.
(7) Kaminsky, W.; Noll, A. Polymerization of Phenyl-Substituted Cyclic Olefins with Metallocene/Aluminoxane Catalysts. In *Ziegler Catalysts, Recent Scientific Innovations and Technological Improvements*; Fink, G., Mülhaupt, R., Brintzinger, H.-H., Eds.; Springer: Berlin, Heidelberg, and New York, 1995.
(8) Noll, A. Dissertation, Universität Hamburg, Germany, 1993.
(9) Kaminsky, W.; Engehausen, R.; Kopf, J. *Angew. Chem.* **1995,** *107*, 2469.
(10) Woo, T. K.; Fan, L.; Ziegler, T. *Organometallics* **1994**, *13*, 2252.
(11) Lohrenz, J. C. W.; Woo, T. K.; Fan, L.; Ziegler, T. *J. Organomet. Chem.* **1995,** *497*, 91.
(12) Woo, T. K.; Margl, P. M.; Lohrenz, J. C. W.; Ziegler, T. *Polym. Mater. Sci. Eng.* **1996,** *74*, 393.
(13) *Polypropylene and other Polyolefins*; van der Ven, S., Ed.; Elsevier: Amsterdam, 1990; p 413.
(14) Huang, J.; Rempel, G. L. *Prog. Polym. Sci.* **1995,** *20*, 459.
(15) Kortmann, K.; Brintzinger, H. H. *New J. Chem.* **1992,** *16*, 51.
(16) Burger, P.; Hortmann, K.; Brintzinger, H. H. *Makromol. Chem., Macromol. Symp.* **1993,** *66*, 127.
(17) van der Leek, Y. Dissertation, Heinrich-Heine-Universität Düsseldorf, Germany, 1996.
(18) Ruchatz, D.; Fink, G. (manuscript in preparation).

MA9710444