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Ethene−Norbornene Copolymerization with Homogeneous Metallocene and Half-Sandwich Catalysts: Kinetics and Relationships between Catalyst Structure and Polymer Structure. 3. Copolymerization Parameters and Copolymerization Diagrams

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ABSTRACT: The copolymerization parameters of the ethene−norbornene copolymerization using various metallocene and half-sandwich catalysts were determined on the basis of composition data with linear graphical methods: Aside from r_1 and r_2, values for r_{11} and r_{21} could be determined in the case of alternating copolymerizations. In this connection, r_{21} differs significantly from catalyst to catalyst and reflects the different tendency of each catalyst to produce copolymers with an alternating monomer sequence. The maximum norbornene contents in the copolymer could be achieved by use of sterically less hindered metallocene catalysts. As an exception to this, the half-sandwich catalysts produced copolymers with surprisingly low norbornene contents.

Introduction

In our previous two papers belonging to this series,[1,2] we have presented the results of the kinetic measurements of the copolymerization process by utilizing different metallocene and half-sandwich catalysts and the interpretation of the ^{13}C NMR copolymer spectra. Aside from differences in the catalytic activity of the catalysts tested, it was found that the copolymer microstructure is dependent on the catalyst structure. In this paper, we present the copolymerization parameters and diagrams.

Experimental Section

For a description of the copolymerization procedure, refer to the first of four papers in this issue.[1]

Polymer Characterization. The melting point or glass-transition temperature of the copolymers was measured on a Mettler-Toledo DSC 820, under a nitrogen atmosphere. For an exact measuring of the glass-transition temperature, the samples were first totally melted and then gradually cooled; the heating and cooling rate was 10 K min^{-1}. The temperature interval of the reheat reached from 0 to 300 °C. With the help of the ^{13}C NMR spectroscopy the norbornene content in the copolymer was determined and correlated with the measured glass-transition temperatures. Conversely, with the help of this correlation function, the norbornene content in the copolymer could be determined by utilizing the following linear relationship: mol % norbornene = $(T_G/4) + 14$. The type of distribution of the norbornene units in the copolymer chain showed no significant influence on the glass-transition temperature.

For a description of the ^{13}C NMR experiments of the copolymers and the calculation of the norbornene content in the copolymer, refer to the second of four papers in this issue.[2]

Results and Discussion

Determination of the Copolymerization Parameters on the Basis of the Copolymer Composition. The copolymerization parameters were determined by applying the linear method introduced by Kelen and Tüdös.[3−5] This procedure, in the following text termed as the KT1 method, is based on the classical Mayo−Lewis equation.[6] In this model, only the monomer last inserted influences the insertion of the following monomer (Markov model first order). In the case of the Markov model second order, the influence of the two monomers inserted last is considered.[7]

Table 1. Copolymerization Parameters for the Ethene−Norbornene Copolymerization in Toluene at 70 °C

catalyst	r_1	r_2	r_1r_2
^{i}Pr[IndCp]ZrCl$_2$	0.88	0.05	0.044
^{i}Pr[(Me-Cp)Ind]ZrCl$_2$	1.14	0.10	0.114
^{i}Pr[(3-^{t}Bu-Cp)Ind]ZrCl$_2$	1.1	0.026	0.029
MeCH[Cp]$_2$ZrCl$_2$	0.83	0.29	0.24
^{i}Pr[FluCp]ZrCl$_2$	1.3	0.03	0.039

In the case of an alternating copolymer with no norbornene microblocks follows $r_{22} = r_{12} = 0$. The copolymerization equation for the Markov model second order simplifies to[7,8]

$$\frac{m_1}{m_2} = 1 + r_{21}\frac{M_1}{M_2}\frac{r_{11}M_1 + M_2}{r_{21}M_1 + M_2}$$

In the case of $r_{22} = r_{12} = 0$, the copolymerization parameters r_{11} and r_{21} can be determined by using the linear method from Kelen and Tüdös,[9] which is here termed the KT2 method.

As shown in the second of four papers in this issue,[2] the catalysts can be divided in two categories depending on the copolymer structure produced, which either contains directly neighboring norbornene units or is of an alternating type. In the case of norbornene microblocks, the KT1 method was used for the determination of the copolymerization parameters (Table 1), and in the case of an alternating copolymer, the KT2 method was used (Table 2). Additionally, we present the corresponding copolymerization diagrams (Figures 1−3), which were the basis for the calculation of the copolymerization parameters listed here.

As mentioned above, the copolymerization parameters shown in Table 1 were based on the Markov model first

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Table 2. Copolymerization Parameters for the Ethene−Norbornene Copolymerization in Toluene at 70 °C[a]

catalyst	r_{11}	r_{21}
^{i}Pr[(3-Me-Cp)Flu]ZrCl$_2$	1.2	3.6
^{i}Pr[(3-^{i}Prop-Cp)Flu]ZrCl$_2$	2.2	2.7
^{i}Pr[(3-^{t}Bu-Cp)Flu]ZrCl$_2$	2.2	8.9
Me$_2$Si[(3-^{t}Bu-Cp)Flu]ZrCl$_2$	5.2	18.2
Me$_2$Si[Me$_4$CpN^{t}Bu]TiCl$_2$	2.2	54

[a] Markov model second order with $r_{22} = r_{12} = 0$.

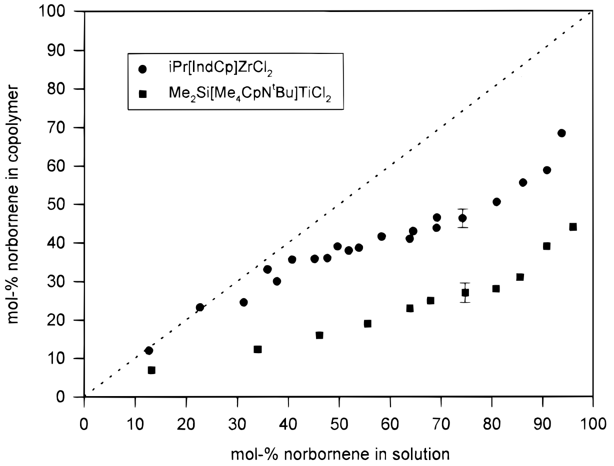

Figure 1. Copolymerization diagram of the ethene−norbornene copolymerization with (●) ^{i}Pr[IndCp]ZrCl$_2$ and (■) Me$_2$Si[Me$_4$CpN^{t}Bu]TiCl$_2$ in toluene at 70 °C.

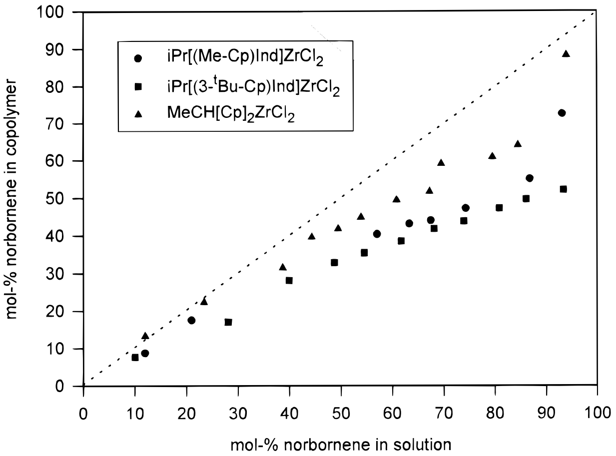

Figure 2. Copolymerization diagram of the ethene−norbornene copolymerization with (●) ^{i}Pr[(Me-Cp)Ind]ZrCl$_2$, (■) ^{i}Pr[(3-^{t}Bu-Cp)Ind]ZrCl$_2$, and (▲) MeCH[Cp]$_2$ZrCl$_2$ in toluene at 70 °C.

order and, therefore, are of limited validity. However, tendencies are reflected in a correct manner. According to this, the maximum norbornene contents in the copolymer could be achieved by applying the MeCH[Cp]$_2$ZrCl$_2$ catalyst. On the other hand, the ^{i}Pr[(3-^{t}Bu-Cp)Ind]ZrCl$_2$ catalyst produces copolymers with the least norbornene content: The r_2-value is more than 10-fold smaller than the r_2 value of the MeCH[Cp]$_2$ZrCl$_2$ catalyst. The copolymerization parameters of the ^{i}Pr[FluCp]ZrCl$_2$ catalyst differ only slightly in comparison with the values of the ^{i}Pr[(3-^{t}Bu-Cp)Ind]ZrCl$_2$ catalyst, and differences in the norbornene content appear only at high monomer concentration ratios of [norbornene]/[ethene] in solution: In that case, the copolymers, produced with the ^{i}Pr[FluCp]ZrCl$_2$ catalyst contain more than 50 mol % norbornene, whereas the copolymers, which were produced with the ^{i}Pr[(3-^{t}Bu-Cp)Ind]ZrCl$_2$ catalyst, contain only a little above 50 mol %. This result was expected, due to the results of the NMR analysis of the copolymers: The ^{i}Pr[(3-^{t}Bu-Cp)Ind]ZrCl$_2$ catalyst produces ethene−norbornene copolymers that contain norbornene blocks with a maximum length of 2. This means that after insertion of two norbornene units, only ethene can be added as the succeeding monomer unit, and as a result of this, $k_{222} = 0$ and therefore $r_{22} = 0$.

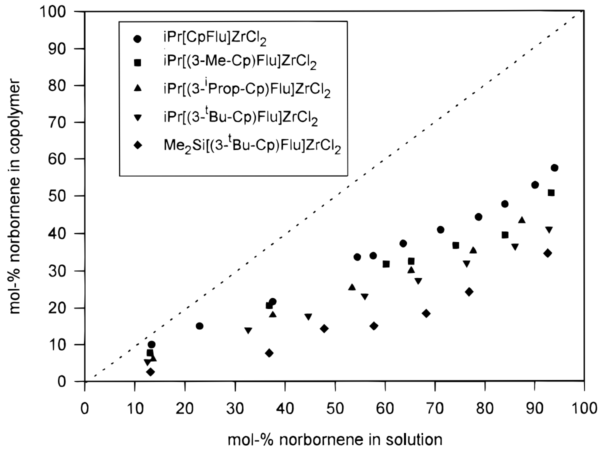

Figure 3. Copolymerization diagram of the ethene−norbornene copolymerization with ^{i}Pr[(3-R-Cp)Flu]ZrCl$_2$ in toluene at 70 °C.

The catalysts listed in Table 2 produce copolymers, which contain no norbornene blocks at all. In this case the following can be concluded: $r_{22} = r_{12} = 0$, as mentioned above, and the copolymerization parameters r_{11} and r_{21} could be determined by the KT2 method. The r_{21} value differs much more from catalyst to catalyst than the r_{11} value: The smallest r_{21} values show ^{i}Pr[3-Me-Cp)Flu]ZrCl$_2$ and ^{i}Pr[3-^{i}Prop-Cp)Flu]ZrCl$_2$; the half-sandwich catalyst Me$_2$Si[Me$_4$CpN^{t}Bu]TiCl$_2$ has the maximum r_{21} value. This result complies with the analysis of the copolymer spectra: The catalysts of the type ^{i}Pr[(3-R-Cp)Flu]ZrCl$_2$ show the strongest tendency for producing ethene-norbornene copolymers with an alternating monomer sequence. The r_{21} value, which is defined to be k_{211}/k_{212}, can be regarded as an indicator for the frequency of alternating monomer sequences in the copolymer: The lower r_{21}, the stronger is the tendency to produce a copolymer with an alternating structure; this of course is only valid by the assumption that $r_{22} = r_{12} = 0$. These results, concerning the alternating tendency, agree with the results of the NMR analysis of the ethene−norbornene copolymers.

The copolymerization behavior of the half-sandwich catalysts Me$_2$Si[Me$_4$CpNCH(CH$_3$)-1-naphthyl]TiCl$_2$ and C$_2$H$_4$[Me$_4$CpNMe$_2$]Cr(η^1,η^1-C$_4$H$_8$) were not extensively tested, but under similar reaction conditions, the norbornene contents in the copolymer were comparable to those that were produced with the Me$_2$Si[Me$_4$CpN^{t}Bu]TiCl$_2$ catalyst.

Determination of the Copolymerization Parameters by Triad Analysis of the NMR Spectra. The NMR spectrum of a copolymer holds a lot of information other than the simple copolymer composition: In the case of a completely known triad distribution, the copolymerization parameters can indirectly be determined by adaption of the triad distribution (Markov first and second order) to the experimental triad distribution with the help of a computer program, which varies the possible reaction probabilities. This method allows the decision whether the Markov model first or second order is valid and, furthermore, the determination of the "true" copolymerization parameters. This procedure was successfully applied in our group to different ethene−α-olefin copolymers,[10−12] because the assignments of the resonances in the NMR spectra of these copolymers to the triads are literature-known.[13] In the case of the ethene−norbornene copolymers, we made an attempt to assign the different NMR signals to the triads, which was only partly successful. A complete triad analysis, as described above, unfortunately requires the complete assignment of the E- and N-centered triads or pentads. Therefore, the copolymerization parameters could not be determined by this method and no decision has yet been made whether the Markov model 1 or 2 is valid here. Further problems are the overlapping signals of the ethene unit and C5/C6 of the norbornene around 30 ppm in the ^{13}C NMR spectra of the copolymers, which makes a triad analysis still impossible, even in the case of a completely known assignment of the triad resonances. To overcome some of these problems, we recently started copolymerization experiments using ^{13}C-enriched monomers and the synthesis of model compounds; the results of these experiments will be the topic of a forthcoming publication.[14]

References and Notes

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