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Copolymerization of Ethene/1-Dodecene and Ethene/1-Octadecene with the Stereorigid Zirconium Catalyst Systems iPr[FluCp]ZrCl$_2$/MAO and Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO: Influence of the Comonomer Chain Length[‡,§]

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ABSTRACT: Ethene was copolymerized with 1-dodecene and 1-octadecene to study the influence of the comonomer chain length on the rate enhancement effect where the catalyst system was stereorigid iPr[FluCp]ZrCl$_2$ (I) or Me$_2$Si[Ind]$_2$ZrCl$_2$ (II) combined with methylaluminoxane (MAO). With catalyst II and both of the comonomers the polymerization rate of ethene increased 2.5-fold before starting to decrease above the [comonomer]/[ethene] ratio of 1. With catalyst I the situation was different. With 1-octadecene the maximum in the curve of the polymerization rate of ethene was again at [comonomer]/[ethene] = 1. With 1-dodecene, on the other hand, the consumption of ethene, instead of decreasing, continued to increase above the [1-dodecene]/[ethene] ratio of 1. The different behavior with the two catalysts and comonomers perhaps is explained by the gap aperture between the π-ligands of the two catalysts and the steric conditions at the catalytic center: the longer the comonomer, and the narrower the gap aperture, the more difficult it is for the ethene monomer unit to insert itself and the ethene propagation reaction becomes slower. The microstructure of the copolymers was investigated with Markovian first- and second-order statistics. The experimental triad distributions can satisfactorily be described with the second-order statistics. The r_{22} and r_{12} parameters obtained show that catalyst I copolymerizes α-olefins better and that, for the same catalyst, there is no marked difference in the values obtained with 1-dodecene and 1-octadecene. Furthermore, the r_{22} parameters were considerably greater with 1-dodecene and 1-octadecene than with 1-hexene. Evidently, a block of the long chain α-olefin opens the gap aperture between the π-ligands, facilitating insertion of an α-olefin. The addition of 1-butene decreased the reactivity of the higher α-olefin: the comonomer content decreased to half with catalyst I and to two-thirds with catalyst II when the 1-butene concentration was increased from 0 to 1 mol/dm^3. Apparently, the synergistic effect works only with heterogeneous catalyst systems and not at all with the homogeneous metallocenes.

Introduction

In recent work we found 1-hexene addition to enhance the rate of ethene consumption in ethene/1-hexene copolymerization with Cp$_2$ZrCl$_2$/MAO,[1] stereorigid iPr[FluCp]ZrCl$_2$/MAO, and stereorigid Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO[2] catalysts and in ethene/1-butene/1-octadecene terpolymerization with Cp$_2$ZrCl$_2$/MAO catalyst.[3] With the Cp$_2$ZrCl$_2$/MAO catalyst the rate enhancement seemed to depend on the heterogeneity of the polymerization: no rate enhancement occurred when the polymer was soluble in the reaction medium. With the stereorigid catalyst systems, the rate enhancement effect of 1-hexene was evident at [1-hexene]/[ethene] ratios under 1. At higher ratios, however, the polymerization rate continued to increase with the iPr[FluCp]ZrCl$_2$/MAO catalyst, but decreased with the Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO catalyst. These systems were homogeneous even at low concentrations of the comonomer.

The reason for the rate enhancement in ethene polymerization upon addition of a comonomer is still unclear, although it has been studied several times during recent years, both with traditional heterogeneous titanium catalysts[4–25] and with homogeneous metallocenes.[1–3,26–31]

The synergistic effect, which may be related to the rate enhancement, has been studied much less widely. Since the first publications almost 10 years ago,[32–34] only a few articles have appeared on the subject.[3,35–37]

In the work reported here ethene was copolymerized with 1-dodecene and 1-octadecene to study the rate enhancement effect of the comonomer in systems polymerized with stereorigid iPr[FluCp]ZrCl$_2$ or Me$_2$Si[Ind]$_2$ZrCl$_2$ catalyst combined with methylaluminoxane (MAO). In addition, terpolymerizations of ethene, 1-butene, and 1-octadecene were made to study the possible synergistic effect occurring upon 1-butene addition.

Experimental Section

Chemicals. iPr[FluCp]ZrCl$_2$ and Me$_2$Si[Ind]$_2$ZrCl$_2$ were synthesized according to Ewen et al.[38] and Herrmann et al.,[39] respectively. Methylaluminoxane was commercially obtained from Witco GmbH as a 10 wt % solution in toluene. Toluene, 1-dodecene, and 1-octadecene were distilled over NaAl(C$_2$H$_4$)$_4$ and stored under argon.

Method of Polymerization. The copolymerizations were performed under argon in a 0.25-dm^3 glass autoclave at 28 °C (25 °C for terpolymerizations) and 2.0-bar ethene overpressure. A propeller-like stirrer was used at 1200 rpm to stir the reaction

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[‡] iPr[FluCp]ZrCl$_2$: isopropylidene[(2,4-cyclopentadien-1-ylidene)-fluoren-9-ylidene]zirconium dichloride. MAO: methylaluminoxane. Me$_2$Si[Ind]$_2$ZrCl$_2$: (dimethylsilylene)bis(η^5-inden-1-ylidene)zirconium dichloride.

[§] Dedicated to Prof. Dr. Dr.es Günther Wilke on the occasion of his 70th birthday.

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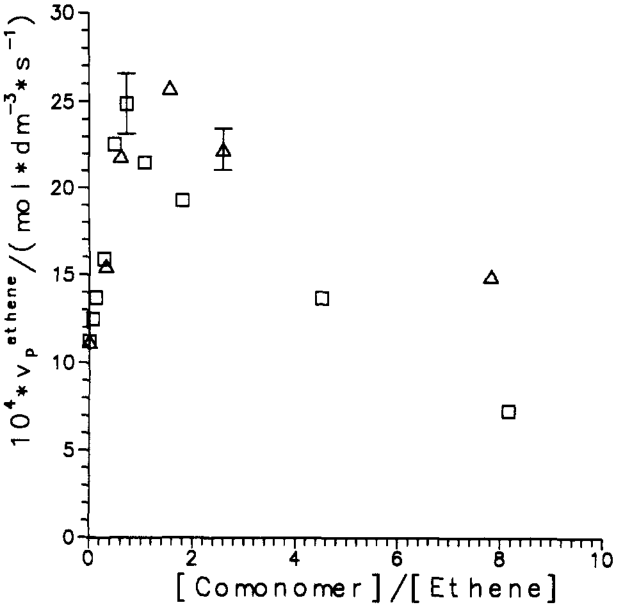

Figure 1. Ethene polymerization rate (v_p^{ethene}) as a function of the [comonomer]/[ethene] ratio in the copolymerization $Me_2Si[Ind]_2ZrCl_2$/MAO catalyst. Polymerization conditions: [Zr] = 5.8×10^{-6} mol/dm^3; [Al]/[Zr] = 3325; t_p = 28 °C; p_{ethene} = 2 bar; solvent, toluene; comonomer (△) 1-dodecene, (□) 1-octadecene.

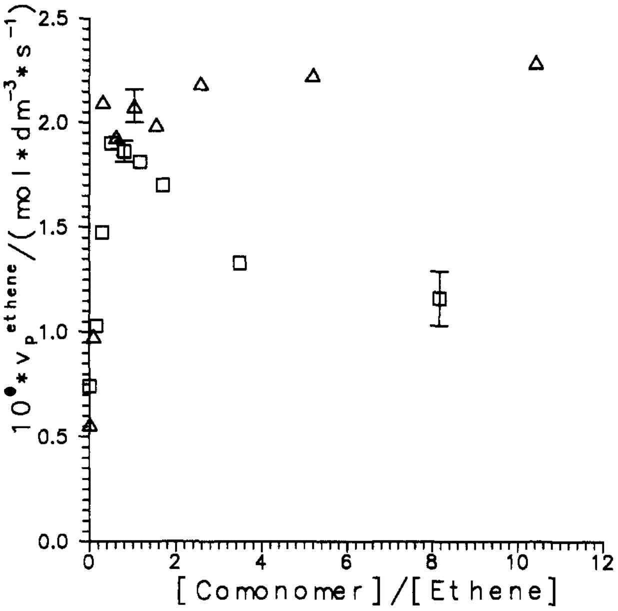

Figure 2. Ethene polymerization rate (v_p^{ethene}) as a function of the [comonomer]/[ethene] ratio in the copolymerization with $iPr[FluCp]ZrCl_2$/MAO catalyst. Polymerization conditions: [Zr] = 1.8×10^{-5} mol/dm^3; [Al]/[Zr] = 2560; t_p = 28 °C; p_{ethene} = 2 bar; solvent, toluene; comonomer (△) 1-dodecene, (□) 1-octadecene.

mixture. The reactor was filled with toluene, comonomer(s), and methylaluminoxane, thermostated, and saturated with monomer gas. The preactivated metallocene solution was then blown with argon overpressure into the reactor (in-situ start) from a funnel, which had been rinsed with a small amount of toluene. The total volume of the liquid phase was 160 cm^3. The pressure of the gaseous monomer was kept constant during the polymerizations by measuring the consumption of the monomer with a mass flow meter and continuously replacing the amount consumed. The time of the polymerization was kept short, so that the conversions of the comonomers were low enough to keep the concentration of the comonomer in the liquid phase as constant as possible. Polymerization was stopped through the addition of CH_3OH, and the reaction mixture was stirred into CH_3OH/HCl. The polymer was filtered, washed with CH_3OH, and dried in vacuum.

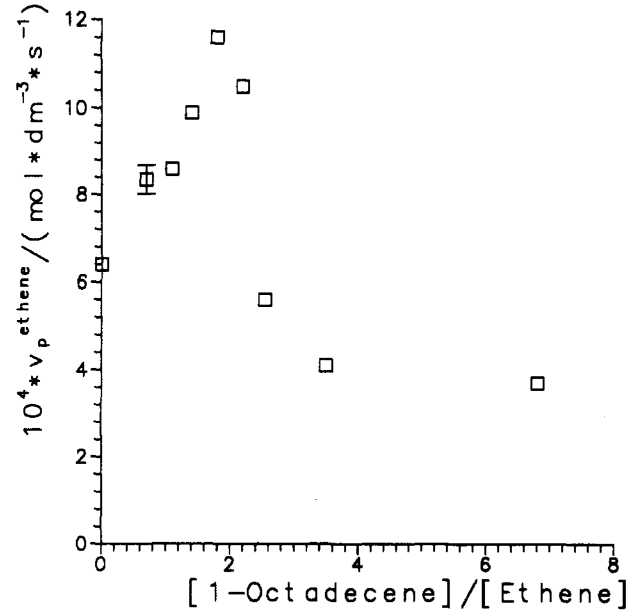

Figure 3. Ethene polymerization rate (v_p^{ethene}) as a function of the [1-octadecene]/[ethene] ratio in the copolymerization with *rac*-$Et[IndH_4]_2ZrCl_2$/MAO catalyst. Polymerization conditions: [Zr] = 4.4×10^{-6} mol/dm^3; [Al]/[Zr] = 6480; t_p = 28 °C; p_{ethene} = 2 bar; solvent, toluene.

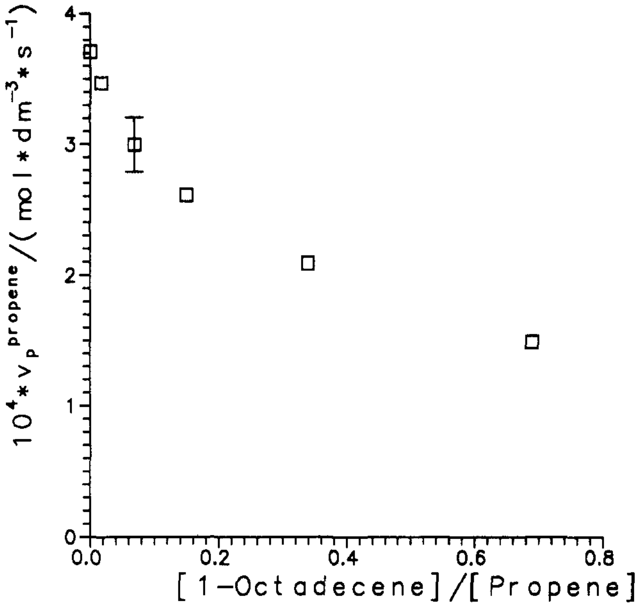

Figure 4. Propene polymerization rate ($v_p^{propene}$) as a function of the [1-octadecene]/[propene] ratio in the copolymerization with $iPr[FluCp]ZrCl_2$/MAO catalyst. Polymerization conditions: [Zr] = 9.7×10^{-6} mol/dm^3; [Al]/[Zr] = 1970; t_p = 25 °C; $p_{propene}$ = 2 bar; solvent, toluene.

Polymer Characterization. The ^{13}C NMR spectra of the co- and terpolymers were recorded with a Bruker WM-300 spectrometer at 120 °C. The sample (500 mg) was dissolved in a 3-cm^3 mixture of 1,2,4-trichlorobenzene and $C_2D_2Cl_4$ (v/v = 3/1). The triad distributions of the copolymers were calculated according to Randall,[40] and the compositions of the terpolymers, according to Seppälä.[32]

Results and Discussion

Copolymerization. Figure 1 shows the dependence of the ethene polymerization rate v_p^{ethene} on the mole ratio [comonomer]/[ethene] in the reaction medium with comonomers 1-dodecene and 1-octadecene and the catalyst system $Me_2Si[Ind]_2ZrCl_2$/MAO. As can be seen, the ethene polymerization rate increased until the [comonomer]/[ethene] ratio was 1. At this point the polymerization rate of ethene, with both comonomers, was 2.5 times the

Table 1. Comparison of the Measured and Calculated Triad Distributions for Selected Ethene (E)/α-Olefin (O) Copolymers (Catalyst: $\mathrm{iPr[FluCp]ZrCl_2/MAO}$)[a]

comonomer	[O]/[E] in solution	model[b]	OOO	EOO + OOE	OEO	EOE	EEO + OEE	EEE	*R*[c]
C_{18}	0.50	exp	0.001	0.001	0.005	0.057	0.125	0.811	
		M1	0.000	0.003	0.004	0.063	0.120	0.810	1×10^{-5}
		M2	0.002	0.002	0.001	0.061	0.123	0.811	7×10^{-6}
C_{18}	0.73	exp	0.003	0.003	0.007	0.067	0.131	0.789	
		M1	0.000	0.005	0.005	0.069	0.131	0.790	8×10^{-6}
		M2	0.003	0.004	0.005	0.069	0.130	0.789	1×10^{-6}
C_{18}	1.74	exp	0.003	0.012	0.028	0.070	0.147	0.740	
		M1	0.001	0.018	0.008	0.076	0.153	0.744	9×10^{-5}
		M2	0.002	0.018	0.018	0.080	0.142	0.740	4×10^{-5}
C_{18}	3.61	exp	0.005	0.022	0.035	0.068	0.068	0.802	
		M1	0.001	0.009	0.002	0.040	0.086	0.862	4×10^{-4}
		M2	0.002	0.007	0.028	0.054	0.058	0.851	1×10^{-4}
C_{12}	0.10	exp	0.000	0.000	0.007	0.016	0.040	0.937	
		M1	0.000	0.003	0.000	0.019	0.040	0.938	1×10^{-5}
		M2	0.000	0.002	0.003	0.020	0.038	0.937	8×10^{-6}
C_{12}	0.31	exp	0.000	0.002	0.005	0.050	0.118	0.825	
		M1	0.000	0.005	0.004	0.057	0.111	0.823	2×10^{-5}
		M2	0.002	0.003	0.000	0.056	0.114	0.825	1×10^{-5}
C_{12}	2.61	exp	0.002	0.016	0.043	0.133	0.244	0.562	
		M1	0.001	0.021	0.027	0.140	0.247	0.564	6×10^{-5}
		M2	0.002	0.021	0.033	0.143	0.239	0.562	4×10^{-5}

[a] Polymerization conditions: see Figure 2. [b] Exp, measured triad distribution (according to ref 40); M1, Markovian statistics of first order; M2, Markovian statistics of second order. [c] *R* = sum of the least squares divided by the number of measured values.

Table 2. Comparison of the Measured and Calculated Triad Distributions for Selected Ethene (E)/α-Olefin (O) Copolymers (Catalyst: $\mathrm{Me_2Si[Ind]_2ZrCl_2/MAO}$)[a]

comonomer	[O]/[E] in solution	model[b]	OOO	EOO + OOE	OEO	EOE	EEO + OEE	EEE	*R*[c]
C_{18}	0.50	exp	0.000	0.000	0.002	0.034	0.074	0.890	
		M1	0.000	0.001	0.001	0.037	0.072	0.889	7×10^{-6}
		M2	0.000	0.001	0.000	0.036	0.073	0.890	2×10^{-6}
C_{18}	0.73	exp	0.002	0.002	0.009	0.046	0.098	0.845	
		M1	0.000	0.009	0.003	0.046	0.097	0.845	2×10^{-5}
		M2	0.001	0.004	0.004	0.050	0.096	0.845	8×10^{-6}
C_{18}	1.81	exp	0.008	0.011	0.019	0.076	0.144	0.742	
		M1	0.001	0.015	0.008	0.077	0.153	0.746	5×10^{-5}
		M2	0.007	0.013	0.015	0.080	0.142	0.742	6×10^{-6}
C_{18}	4.34	exp	0.013	0.017	0.039	0.075	0.124	0.732	
		M1	0.002	0.025	0.008	0.070	0.151	0.744	3×10^{-4}
		M2	0.013	0.020	0.032	0.082	0.121	0.732	2×10^{-5}
C_{12}	0.31	exp	0.000	0.000	0.004	0.030	0.059	0.907	
		M1	0.000	0.000	0.001	0.031	0.060	0.908	5×10^{-5}
		M2	0.000	0.001	0.003	0.031	0.058	0.907	8×10^{-6}
C_{12}	1.04	exp	0.001	0.010	0.016	0.095	0.165	0.713	
		M1	0.000	0.010	0.010	0.092	0.172	0.716	2×10^{-5}
		M2	0.001	0.010	0.017	0.094	0.165	0.713	2×10^{-7}
C_{12}	2.61	exp	0.001	0.012	0.033	0.116	0.195	0.643	
		M1	0.000	0.014	0.017	0.114	0.208	0.647	8×10^{-5}
		M2	0.002	0.014	0.029	0.119	0.193	0.643	5×10^{-6}

[a] Polymerization conditions: see Figure 1. [b] Exp, measured triad distribution (according to ref 40); M1, Markovian statistics of first order; M2, Markovian statistics of second order. [c] *R* = sum of the least squares divided by the number of measured values.

homopolymerization rate. The decay rate above this ratio was faster with the 1-octadecene comonomer.

Figure 2 reveals the dependence of the ethene polymerization rate $\upsilon_p^{\mathrm{ethene}}$ on the [comonomer]/[ethene] ratio in the reaction medium with the same comonomers and the catalyst system $\mathrm{iPr[FluCp]ZrCl_2/MAO}$. As with the $\mathrm{Me_2Si[Ind]_2ZrCl_2/MAO}$ catalyst, the polymerization rate of ethene increased in the presence of 1-octadecene up to a [1-octadecene]/[ethene] ratio of 1, but upon further addition of comonomer it began to decrease. The situation was quite different with the shorter comonomer (1-dodecene): after the concentration of 1-dodecene was increased above the [1-dodecene]/[ethene] ratio of 1, there was no decay in the ethene polymerization rate but instead a slight increase. The same was seen in our previous work[2] with 1-hexene as comonomer, and the increase was even greater there. To summarize, with the $\mathrm{iPr[FluCp]ZrCl_2/MAO}$ catalyst, above the [comonomer]/[ethene] ratio of 1 the polymerization rate of ethene (i) increases markedly with 1-hexene (C_6), (ii) increases slightly with 1-dodecene (C_{12}), and (iii) decreases with 1-octadecene (C_{18}).

The reason for the different behavior perhaps lies in the steric conditions of the catalytic center: the longer the comonomer, the more difficult it is for the ethene monomer unit to insert itself and the ethene propagation reaction becomes slower.

Figure 3 shows by comparison the dependence of the ethene polymerization rate $\upsilon_p^{\mathrm{ethene}}$ on the mole ratio [1-octadecene]/[ethene] in the reaction medium with the catalyst system *rac*-$\mathrm{Et[IndH_4]_2ZrCl_2/MAO}$. Here the polymerization rate increased steadily to a maximum at the [1-octadecene]/[ethene] ratio of 2. Above this, the rate decreased sharply.

With all three catalysts the copolymers were insoluble in the reaction medium at low concentrations of the comonomer, in contrast to the situation with 1-hexene.[2] The copolymer obtained with the $\mathrm{Et[IndH_4]_2ZrCl_2/MAO}$ catalyst was insoluble in toluene until the [1-octadecene]/[ethene] ratio reached 2. Above this ratio it dissolved in the reaction medium, which then became gel-like.

Figure 4 shows the propene polymerization rate $\upsilon_p^{\mathrm{propene}}$ plotted against the mole ratio [1-octadecene]/[propene]

Table 3. Comparison of the Copolymerization Parameters of the Selected Ethene/α-Olefin Copolymers (Calculated from the Second-Order Markovian Statistics) (Catalysts: iPr[FluCp]ZrCl$_2$/MAO (I) and Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO (II))

catalyst	comonomer	r_{11}[a]	r_{21}[a]	r_{22}[a]	r_{12}[a]
I	C_{12}	7.2	5.0	2.9	0.057
I	C_{18}	11.2	6.3	1.6	0.044
II	C_{12}	12.0	5.7	0.3	0.036
II	C_{18}	14.7	8.4	0.4	0.035

[a] Average value of several experiments; 1 = ethene, 2 = comonomer.

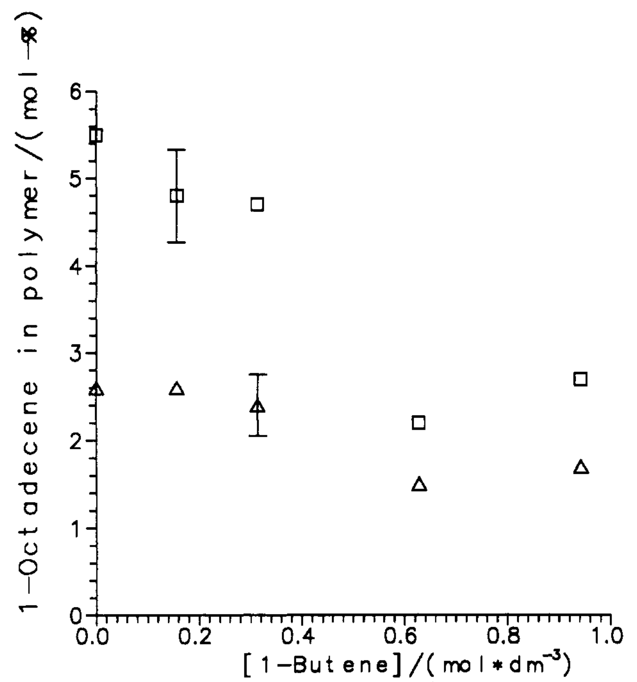

Figure 5. Dependence of the 1-octadecene content in the polymer on the 1-butene concentration in the reaction medium in terpolymerization with different catalysts. Polymerization conditions: t_p = 25 °C; p_{ethene} = 1.8 bar; solvent, toluene. Catalysts: (△) Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO, [Zr] = 2.7 × 10^{-6} mol/dm^3, [Al]/[Zr] = 7920; (□) iPr[FluCp]ZrCl$_2$/MAO, [Zr] = 1.8 × 10^{-5} mol/dm^3, [Al]/[Zr] = 2560.

in the reaction medium with catalyst system iPr[FluCp]-ZrCl$_2$/MAO. As can be seen, the addition of comonomer at no point increased the polymerization rate. In explanation of the similar results found earlier for 1-hexene and propene[2] it was suggested that there are no "sleeping" centers in the catalyst to be awakened with the addition of a long chain α-olefin. The rate enhancement effect in the ethene/1-hexene system was correspondingly attributed to the increase in the active species due to the addition of α-olefin.

The experimental monomer triad distributions, as well as the calculated triad distributions according to Markovian first- and second-order statistics, are shown in Tables 1 and 2. The theory and the equations have been presented earlier.[2] With both catalyst systems, the second-order statistic gives a better fit to the data. This means that the insertion of a monomer into the polymer chain is controlled by the last two monomer units at the end of the growing chain.

The information in Table 3 is now discussed in more detail, as an analysis of the r parameters reveals some interesting features.

(i) The α-olefin insertion into the growing polymer chain is more favorable with the iPr[FluCp]ZrCl$_2$/MAO than the Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO catalyst, perhaps, because of the broader coordination gap aperture between the π-ligands, as discussed earlier for 1-hexene.[2]

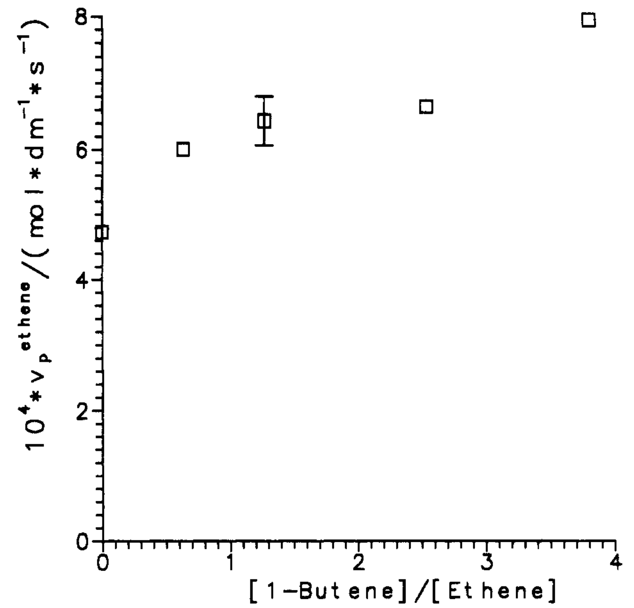

Figure 6. Ethene polymerization rate (v_p^{ethene}) as a function of the [1-butene]/[ethene] ratio in the terpolymerization of ethene, 1-butene, and 1-octadecene with Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO catalyst. Polymerization conditions: [Zr] = 2.7 × 10^{-6} mol/dm^3; [Al]/[Zr] = 7920; t_p = 25 °C; p_{ethene} = 1.8 bar; solvent, toluene; [1-octadecene] = 0.1 mol/dm^3.

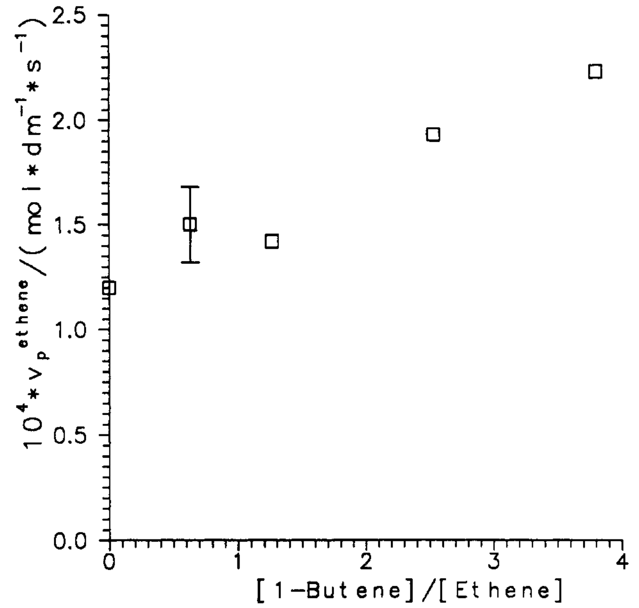

Figure 7. Ethene polymerization rate (v_p^{ethene}) as a function of the [1-butene]/[ethene] ratio in the terpolymerization of ethene, 1-butene, and 1-octadecene with iPr[FluCp]ZrCl$_2$/MAO catalyst. Polymerization conditions: [Zr] = 1.8 × 10^{-5} mol/dm^3; [Al]/[Zr] = 2560; t_p = 25 °C; p_{ethene} = 1.8 bar; solvent, toluene; [1-octadecene] = 0.1 mol/dm^3.

(ii) The validity of point i is clearly seen in the r_{22} parameters, which describe the case where a long chain α-olefin is inserted into the sequence {R—(α-olefin)—(α-olefin)—catalyst}. The values of the parameter are much higher for the iPr[FluCp]ZrCl$_2$/MAO catalyst than for the Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO catalyst: 10 times as high with 1-dodecene and 4 times as high with 1-octadecene.

(iii) A comparison of the r_{22} and r_{12} parameters shows that it is more probable that a 1-octadecene monomer unit is added to the sequence {R—(α-olefin)—(α-olefin)—catalyst} than to the sequence {R—(ethene)—(α-olefin)—catalyst}.

(iv) There is no marked difference between the r parameters obtained for the same catalyst system with 1-dodecene and 1-octadecene.

(v) The r_{11} and r_{21} parameters reveal a greater tendency for an ethene monomer unit to be added to the sequence {R—(ethene)—(ethene)—catalyst} than into the sequence {R—(α-olefin)—(ethene)—catalyst} ($r_{11} > r_{21}$). With 1-hexene as comonomer the values of the parameters are nearly the same ($r_{11} \sim r_{21}$).[2]

(vi) A comparison of the present r_{22} parameters with those of the previous work[2] with 1-hexene shows that, for the iPr[FluCp]$ZrCl_2$/MAO catalyst, the value of the parameter is 10 times as high with 1-dodecene as comonomer as with 1-hexene. For the $Me_2Si[Ind]_2ZrCl_2$/MAO catalyst the difference is even greater. Earlier it was proposed that a long block of α-olefin at the end of a growing polymer chain forces the π-ligands into a more open arrangement, making the insertion of α-olefin easier.[2] Now, it could be added to this that a longer α-olefin opens the π-ligands wilder than a shorter α-olefin. This interpretation receives support in the higher value of the r_{22} parameter obtained with 1-dodecene and 1-octadecene than with 1-hexene.

Terpolymerization. Figure 5 illustrates the dependence of the 1-octadecene content in the terpolymer on the 1-butene concentration in the feed: the more 1-butene in the feed, the less 1-octadecene the terpolymer contained. When the 1-butene concentration was increased from 0 to 1 mol/dm^3, the 1-octadecene content decreased from 5.5 to 2.5 mol % with the iPr[FluCp]$ZrCl_2$/MAO catalyst and from 2.6 to 1.7 mol % with the $Me_2Si[Ind]_2ZrCl_2$/MAO catalyst. The same effect was seen in the earlier work with the Cp_2ZrCl_2/MAO catalyst.[3]

Although the content of the long chain α-olefin decreased with 1-butene addition, the consumption of ethene increased continuously. At a 1-octadecene concentration of 0.1 mol/dm^3 ([1-octadecene]/[ethene] = 0.37), the consumption of ethene was not at a maximum, as can be seen in Figures 6 and 7, and further addition of α-olefin increased the consumption of ethene. Surprisingly, the consumption of ethene did not pass through a maximum as in the copolymerization of ethene and 1-octadecene (Figures 1 and 2) but continued to increase instead.

As indicated in the earlier studies,[3,36] the synergistic effect evidently works only with heterogeneous catalyst systems and not at all with the homogeneous metallocenes.

References and Notes

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