Observations on the Synergistic Effect of Adding 1-Butene to Systems Polymerized with $MgCl_2/TiCl_4$ and Cp_2ZrCl_2 Catalysts

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ABSTRACT: Ethene was copolymerized with 1-decene and 1-hexadecene in the presence of heterogeneous $MgCl_2/TiCl_4$-triethylaluminum catalyst to study the effect of adding 1-butene to the polymerization system. When 1-butene concentration in the feed was increased from 0 to 0.4 mol/dm^3, 1-decene content in the polymer increased 2-fold. Further addition of 1-butene has no effect. The more reactive the added comonomer, the more it increased the ethene consumption. Ethene was also copolymerized with 1-octadecene in the presence of Cp_2ZrCl_2-methylaluminoxane catalyst. Surprisingly, 1-butene addition decreased the reactivity of the higher α-olefin: 1-octadecene content decreased linearly, to one-third, when 1-butene concentration was increased from 0 to 1 mol/dm^3. Monitoring of the ethene consumption during the polymerizations showed that the comonomer concentration in the feed has a saturation point, beyond which further addition of comonomer does not increase the consumption of ethene.

Introduction

It is well-known that when 1-butene is added to a polymerization system containing ethene and higher α-olefin, e.g., 1-hexadecene, the content of the higher α-olefin in the polymer increases. This synergistic effect has been observed with both $TiCl_3$[1-3] and $MgH_2/TiCl_4$[4-6] catalysts.

In our previous work[7] the activity increase upon 1-hexene addition was studied with metallocene catalyst. In the present work the synergistic effect was investigated on a system containing ethene, 1-butene, and long chain α-olefins (C_{10}, C_{16}, or C_{18}), with both Cp_2ZrCl_2 and $MgCl_2/TiCl_4$ catalysts. Ethene consumption was also monitored continuously and products were determined.

Experimental Section

Apparatus and Method of Polymerization. Polymerizations were performed in *n*-heptane in a 0.5-dm^3 stainless steel reactor at 70 °C and 2.5 bar ethene overpressure for $MgCl_2/TiCl_4$ catalyst and 30 and 70 °C and 1.5 bar overpressure for Cp_2ZrCl_2 catalyst. The stirring speed, with a propeller-like stirrer, was 800 rpm.

n-Heptane (300 cm^3) was introduced into the evacuated and N_2-purged reactor, after which the comonomers were added batchwise, 1-decene, 1-hexadecene, and 1-octadecene with a pump and 1-butene through a flowmeter. The cocatalyst solution was pumped into the reactor at the polymerization temperature, and the ethene feed was started. Consumption of ethene was followed with a mass flow controller connected to a computer with acquisition frequency of 1 Hz. After equilibrium was reached, polymerization was initiated by pumping the Cp_2ZrCl_2 catalyst/toluene solution into the reactor. Titanium catalyst/*n*-heptane slurry was blown into the reactor from a funnel with nitrogen. The partial pressure of ethene was maintained constant with an electronic pressure controller and a solenoid valve, and the reactor temperature was controlled with a thermostat connected to a Pt-100 resistance thermometer. The pressure control was accurate to within ±0.03 bar and the reactor temperature to within ±0.1 °C. Concentration of 1-butene in *n*-heptane was calculated according to Kissin.[8] The conversions of the comonomers were kept low in order to maintain the concentrations as constant as possible.

After polymerization, the reactor was degassed, the reaction medium was washed with diluted hydrochloric acid and water, and *n*-heptane was evaporated gently. The residue was stirred with acetone overnight to extract the unpolymerized high-boiling comonomers, after which it was filtered and dried in vacuum at 70 °C overnight.

Chemicals. The heterogeneous catalyst was a supported Ziegler-Natta catalyst of type $MgCl_2/TiCl_4$ without donors made by ball milling with the titanium content 7 wt%; the triethylaluminum was 10 wt% solution in *n*-heptane (from Schering AG). The metallocene, Cp_2ZrCl_2, catalyst was from Aldrich-Chemie and methylaluminoxane, from Witco GmbH, was 10 wt% in toluene.

n-Heptane was grade GR from J.T. Baker, ethene was grade 2.7 and 1-butene 2.0, both from AGA, 1-decene, and 1-hexadecene were from Merck, and 1-octadecene was from Aldrich-Chemie. All materials were further purified by flowing them through columns containing CuO and Al_2O_3.[9]

Polymer Characterization. DSC curves were obtained from powder form (4.5 ± 0.2 mg) samples. Starting temperature was 0 °C, heating rate 10 °C/min, and end temperature 180 °C. Samples were heated twice, and between the runs were cooled at a rate of 10 °C/min. The crystallinities were determined from melting range integrals from the second curve using 290 J/g as heat of fusion.

Molar masses were investigated with a Waters high-temperature GPC device equipped with three TOSOH mixed bed columns with exclusion limit for polystyrene 4×10^8. Solvent 1,2,4-trichlorobenzene was used at a flow rate of 1.0 cm^3/min. The columns were calibrated universally with broad-molar-mass-distribution linear low-density polyethenes.

The monomer content of the polymers was determined with a Varian 400 Unity nuclear magnetic spectrometer according to Seppälä.[1] Because some of the polymers had low molar masses the end methyl groups were not used in the calculations.

Results and Discussion

$MgCl_2/TiCl_4$ Catalyst. The polymerization conditions and the properties of the polymers obtained with the $MgCl_2/TiCl_4$ catalyst are set out in Table 1 and 2.

As can be seen in Figure 1a, when a small amount of comonomer was added the activity increased, and the smaller the comonomer the more the activity increased. With 1-hexadecene as comonomer, there was a slight decrease in activity above 0.5 mol/dm^3.

Terpolymerizations were performed with a constant concentration long chain α-olefin and increasing concentration of 1-butene. Figure 1b reveals that even though addition of the long chain α-olefin beyond a concentration of 0.5 mol/dm^3 did not increase the ethene consumption (Figure 1a); addition of 1-butene continued to increase the ethene consumption.

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Table 1. Polymerizations of Ethene, 1-Butene, and 1-Decene with $MgCl_2/TiCl_4$ Catalyst[a]

	1-butene		1-decene						
run	in reactor, mol/dm³	in polymer, wt %	in reactor, mol/dm³	in polymer, wt %	yield of polymer, g	X_c, %	T_m, °C	$\bar{M}_w$, 10^3 g/mol	$\bar{M}_w/\bar{M}_n$
1	0	0	0.16	4.6	5.0	34	127.2	nd[c]	nd[c]
2	0.24	3.5[b]	0.16	6.8[b]	9.9[b]	27	124.2	391	8.9
3	0.39	6.9	0.16	9.7	11.7	16	120.3	320	8.5
4	0.53	9.9	0.16	9.4	13.5	7	119.8	241	7.8
5	0.72	13.0	0.16	9.2	14.8	3	121.5	207	7.8
6	0.92	15.5	0.16	7.6	16.0	2	120.9	204	8.6

[a] t = 60 °C, $p(C_2H_4)$ = 2.5 bar, Ti = 0.18 mmol, Al = 36 mmol (as TEA). [b] Average of three runs. [c] Not detected = nd.

Table 2. Polymerizations of Ethene, 1-butene, and 1-Hexadecene with $MgCl_2/TiCl_4$ Catalyst[a]

	1-butene		1-hexadecene						
run	in reactor, mol/dm³	in polymer, wt %	in reactor, mol/dm³	in polymer, in wt %	yield of polymer, g	X_c, %	T_m, °C	$\bar{M}_w$, 10^3 g/mol	$\bar{M}_w/\bar{M}_n$
7	0	0	0.47	0.7[b]	2.0[b]	43	133.8	nd[c]	nd[c]
8	0.24	2.2	0.47	0.6	3.8	32	122.6	513	4.9
9	0.39	5.2	0.47	0.8	6.2	26	119.3	469	6.8
10	0.53	7.5	0.47	1.2	9.2	15	121.2	363	6.5
11	0.72	12.7	0.47	1.6	10.5	3	120.8	361	7.6
12	0.92	12.0	0.47	1.1	10.8	2	120.5	361	8.4

[a] t = 60 °C, $p(C_2H_4)$ = 2.5 bar, Ti = 0.18 mmol, Al = 36 mmol (as TEA). [b] Average of two runs. [c] Not detected = nd.

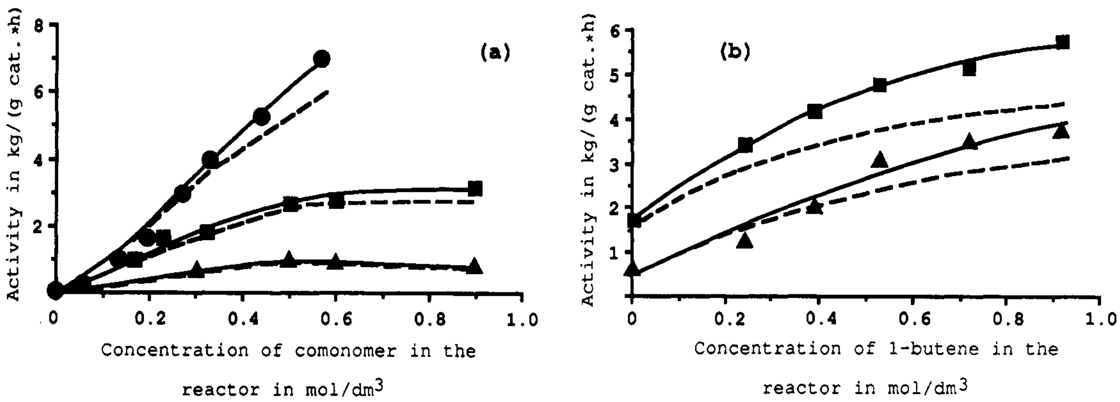

Figure 1. Co- and terpolymerization of ethene, 1-butene, 1-decene, and 1-hexadecene: t = 60 °C, $p(C_2H_4)$ = 2.5 bar, Ti = 0.18 mmol, Al = 36 mmol (as TEA); (a) copolymerization of ethene and 1-butene, 1-decene, or 1-hexadecene; (b) terpolymerization [1-decene or 1-hexadecene] = 0.5 mol/dm³; (●) 1-butene, (■) 1-decene, (▲) 1-hexadecene, (—) total activity, (- -) activity for ethene.

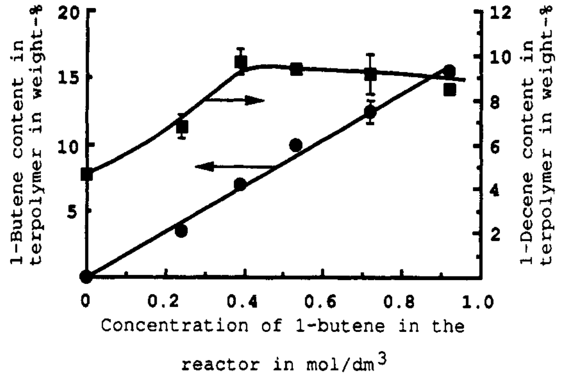

Figure 2. Terpolymerization of ethene, 1-butene, and 1-decene with $MgCl_2/TiCl_4$ catalyst: t = 60 °C, $p(C_2H_4)$ = 2.5 bar [1-decene] = 0.5 mol/dm³, Ti = 0.18 mmol, Al = 36 mmol (as TEA); (●) 1-butene content in terpolymer and (■) 1-decene content in terpolymer.

As can be seen in Figure 2 in the region where the consumption of ethene increased with 1-butene addition, the reactivity of 1-decene could be increased 2-fold. As depicted in Figure 3, the same was true for 1-hexadecene. Table 1 shows that the molar mass decreased when the concentration of 1-butene was increased in the feed. The reason could be that the comonomer acts here as a chain transfer agent.

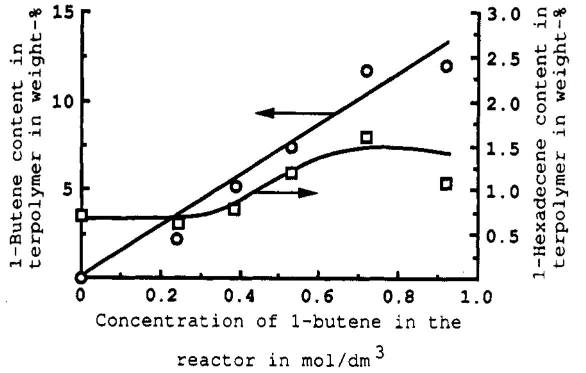

Figure 3. Terpolymerization of ethene, 1-butene, and 1-hexadecene with $MgCl_2/TiCl_4$ catalyst: t = 60 °C, $p(C_2H_4)$ = 2.5 bar [1-hexadecene] = 0.5 mol/dm³, Ti = 0.18 mmol, Al = 36 mmol (as TEA); (○) 1-butene content in terpolymer and (□) 1-hexadecene content in terpolymer.

Cp_2ZrCl_2 Catalyst. The polymerization conditions and the properties of the polymers obtained with the Cp_2ZrCl_2 catalyst are set out in Table 3 and 4. Besides 70 °C, polymerizations were performed at 30 °C, where the polymer was less soluble.

As Figure 4 shows even long chain α-olefins increased the ethene consumption. Figure 4 also reveals that the consumption increases up to a maximum value at 0.1 mol/dm³, before falling off slightly. The maximum consump-

Table 3. Polymerizations of Ethene, 1-Butene, and 1-Octadecene with Cp_2ZrCl_2 Catalyst^a

	1-butene		1-octadecene						
run	in reactor, mol/dm^3	in polymer, wt%	in reactor, mol/dm^3	in polymer, wt%	yield of polymer, g	X_c,^{b} %	T_m, °C	$\bar{M}_w$, 10^3 g/mol	$\bar{M}_w/\bar{M}_n$
13	0	0	0.10	12.0	2.0	33	121.3	107	2.1
14	0.21	1.4	0.10	9.6	1.8	27	111.9	91	2.1
15	0.41	7.0	0.10	9.6	2.9	20	97.9	64	2.0
16	0.41	6.9	0.10	7.2	2.1	20	99.2	61	2.0
17	0.62	9.0	0.10	7.8	4.0	12	90.1	55	1.9
18	0.82	11.4	0.10	7.7	4.4	10	88.6	66	1.9
19	1.02	12.7	0.10	5.2	4.6	4	86.8	48	2.3

^{a} t = 30 °C, p(C_2H_4) = 1.5 bar, Zr = 3.4×10^{-3} mmol, Al (as MAO) = 6.8 mmol. ^{b} (ΔH_f/291 J/g) × 100.

Table 4. Polymerizations of Ethene, 1-Butene, and 1-Octadecene with Cp_2ZrCl_2 Catalyst^a

	1-butene		1-octadecene						
run	in reactor, mol/dm^3	in polymer, wt%	in reactor, mol/dm^3	in polymer, wt%	yield of polymer, g	X_c,^{b} %	T_m, °C	$\bar{M}_w$, 10^3 g/mol	$\bar{M}_w/\bar{M}_n$
20	0	0	0	0	3.7	53	137.7	89	2.4
21	0	0	0.16	23.3	12.3	23	104.5	14	2.3
22	0.15	3.2	0.16	19.6	12.1	15	94.6	12	2.4
23	0.31	6.7	0.16	20.9	11.1	5	77.0	8	2.5
24	0.42	8.3	0.16	15.4	12.8	4	75.2	8	2.3
25	0.58	12.8	0.16	16.8	13.1	5	60.8	7	2.5
26	0.73	16.5	0.16	11.5	12.5	2	65.1	7	2.3
27	1.02	19.6	0.16	8.0	8.1	1	56.7	6	2.2

^{a} t = 70 °C, p(C_2H_4) = 1.5 bar, Zr = 1.4×10^{-3} mmol, Al (as MAO) = 2.8 mmol. ^{b} (ΔH_f/291 J/g) × 100.

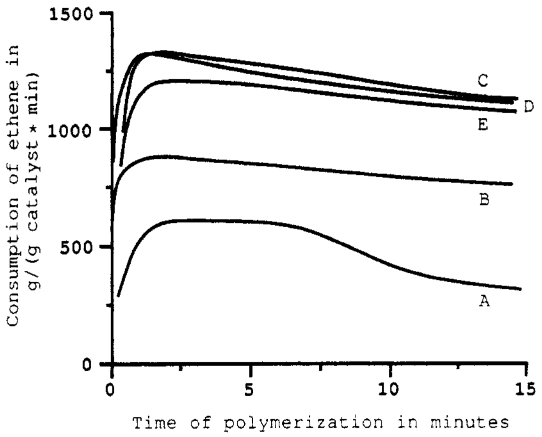

Figure 4. Dependence of ethene consumption on 1-octadecene addition: t = 70 °C, p(C_2H_4) = 1.5 bar, Zr = 1.4×10^{-3} mmol, Al (as MAO) = 2.8 mmol [1-octadecene]; (A) 0 M, (B) 0.02 M, (C) 0.10 M, (D) 0.13 M, and (E) 0.16 M.

tion here seemed to be where the polymer dissolved totally in the reaction medium, which was when the concentration of the α-olefin was 0.13 mol/cm^3. The dissolution was checked by visual inspection: when the reactor was opened, the reaction medium was clear and transparent.

The reason could be the same as discussed with the stereorigid ansa-metallocenes by Herfert et al.[10] In the ethene/1-octadecene copolymerization the concentration of the [R-ethene-(1-octadecene)-cat] active sites, where R is the polymer chain, is increasing with the increasing concentration of 1-octadecene. When the concentration of the comonomer is increased further the concentration of the [R-(1-octadecene)-(1-octadecene)-cat] active centers is increasing. This was seen in the spectra of the samples C–E showed in Figure 5. There the peak at 36.4 ppm corresponds to a structure of EOO or OOE,[11] where E is an ethene monomer unit and O is a 1-octadecene monomer unit. In the spectra run from the samples B the structure could not be seen. The [R-(1-octadecene)-(1-octadecene)-cat] active centers polymerize ethene slower because they are more steric hindered than the ones containing only one 1-octadecene. The reactivity ratios of the monomers calculated with the Finemann–Ross method are $r_E = 55$ and $r_O = 0.008$ for ethene and 1-octadecene, respectively.

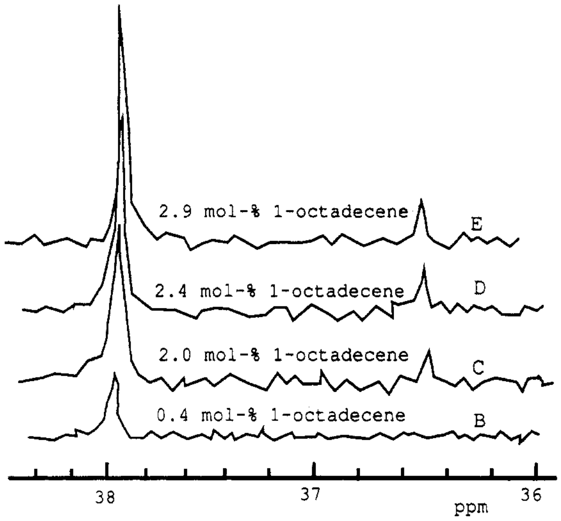

Figure 5. The ^{13}C NMR spectra of the selected ethene/1-octadecene copolymer samples.

The same pattern in the consumption of ethene was evident in polymerization at 30 °C. In this case the concentration of 1-butene was increased, and the concentration of 1-octadecene was kept constant (Figure 6). The maximum consumption was reached at the 1-butene concentration of 0.82 mol/dm^3. At 70 °C (Figure 7) the consumption increased only slightly when 1-butene was present, and further increase in the concentration did not change the consumption. One explanation could be that, at 70 °C, some slight 1-butene incorporation in the polymer and decrease in the molar mass made the polymer soluble in the medium, so that the increase in concentration did not increase the consumption of ethene. It can also be stated that the ethene consumption at 70 °C is 8 times higher than at 30 °C. As shown in an earlier work,[7] the rate enhancement effect was only seen when the polymer was insoluble in the medium. At 30 °C a higher 1-butene incorporation in the polymer was needed to make the polymer dissolve in the medium, and the maximum was

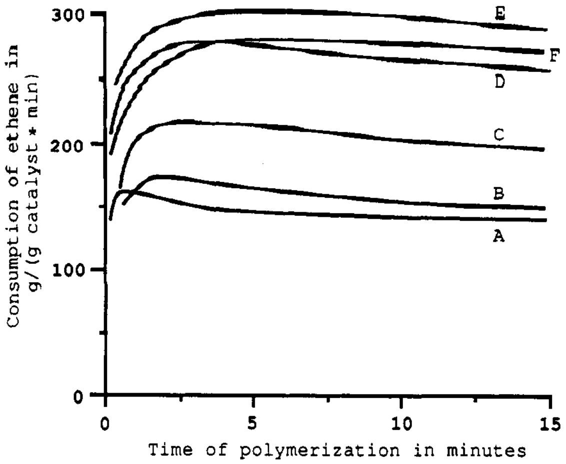

Figure 6. Dependence of ethene consumption on 1-butene addition: t = 30 °C, p(C_2H_4) = 1.5 bar [1-octadecene] = 0.10 M; Zr = 3.4 × 10^{-3} mmol, Al (as MAO) = 6.8 mmol [1-butene]; (A) 0 M, (B) 0.21 M, (C) 0.41 M, (D) 0.62 M, (E) 0.82 M, (F) 1.02 M.

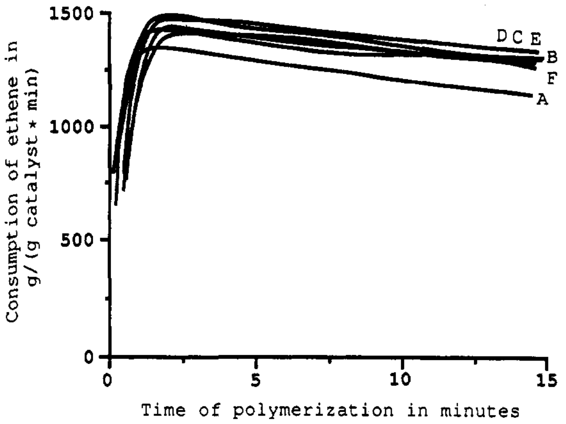

Figure 7. Dependence of ethene consumption on 1-butene addition: t = 70 °C, p(C_2H_4] = 1.5 bar [1-octadecene] = 0.10 M, Zr = 1.4 × 10^{-3} mmol, Al (as MAO) = 2.8 mmol [1-butene]; (A) 0 M, (B) 0.15 M, (C) 0.31 M, (D) 0.42 M, (E) 0.58 M, (F) 0.73 M.

seen at a higher 1-butene concentration. This finding would suggest that the diffusion phenomena plays a role too. Above this concentration the ethene consumption began to decrease, an effect that has also been seen with heterogeneous titanium catalysts.[12,13] Herfert et al.[10] showed in their work that when comonomer was added to the propene polymerization system the consumption of propene decreased and this was explained by the fact that "sleeping" centers were not present in the polymerization. It could be that 1-octadecene wakes up only part of the "sleeping" centers, and then the addition of 1-butene wakes up also the centers that the longer 1-olefin is unable to do and the consumption of ethene increases further. The same phenomena was seen also with the heterogeneous catalyst.

Figures 8 and 9 illustrate the dependence of the 1-octadecene content on the 1-butene concentration in the feed, at both 30 and 70 °C. Surprisingly, the more 1-butene in the feed the less 1-octadecene the polymer contained. The 1-octadecene content decreased from 23 to 8 wt% at 70 °C and from 12 to 5 wt% at 30 °C when 1-butene concentration in the feed was increased from 0 to 1 mol/dm^3. As in the case of activity increase,[10] one explanation may be that the higher the concentration of 1-butene the more there are [R-(1-butene)-cat] active centers, which favor the addition of ethene or 1-butene and thus the amount of 1-octadecene in the polymer is decreased.

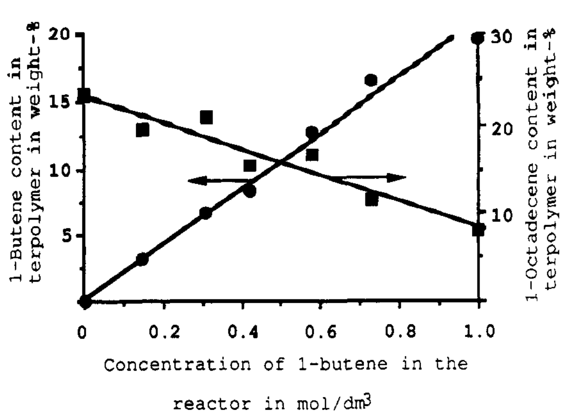

Figure 8. Terpolymerizations of ethene, 1-butene, and 1-octadecene with Cp_2ZrCl_2 catalyst: t = 70 °C, p(C_2H_4) = 1.5 bar, Zr = 1.4 × 10^{-3} mmol, Al (as MAO) = 2.8 mmol [1-octadecene) = 0.10 mol/dm^3; (●) 1-butene content in terpolymer and (■) 1-octadecene content in terpolymer.

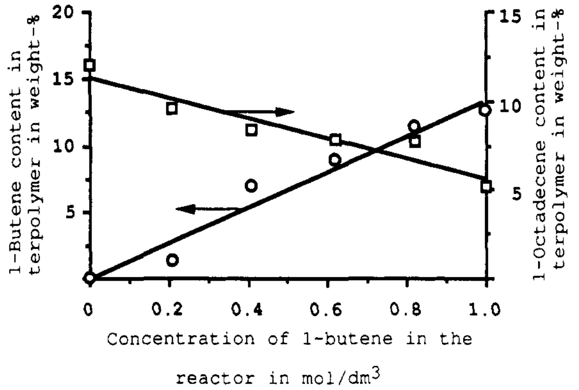

Figure 9. Terpolymerizations of ethene, 1-butene, and 1-octadecene with Cp_2ZrCl_2 catalyst: t = 30 °C, p(C_2H_4) = 1.5 bar, Zr = 3.4 × 10^{-3} mmol, Al (as MAO) = 6.8 mmol [1-octadecene] = 0.16 mol/dm^3; (○) 1-butene content in terpolymer and (□) 1-octadecene content in terpolymer.

Although the content of the long chain α-olefin decreases with 1-butene addition, the consumption of ethene increases to a maximum, as seen in Figures 6 and 7. The reason could be the same as discussed with Figure 4.

Conclusions

A synergistic effect was at work with the traditional heterogeneous $MgCl_2$-supported titanium catalyst, and twice as much 1-decene could be incorporated into the polymer in the presence of 1-butene. The long chain α-olefin (C_{16}) increased the ethene consumption only slightly, and when concentration was increased the activity began to decrease.

With the Cp_2ZrCl_2 catalyst the activity was enhanced with the very long chain α-olefin (C_{18}). THe consumption of ethene was enhanced up to a maximum value, above which it began to decrease, although the concentration of the comonomer was increased.

Terpolymerizations, which were performed with a constant long chain α-olefin concentration and a varying 1-butene concentration, revealed that even when further addition of the long chain α-olefin no longer increased the ethene consumption, the addition of 1-butene continued to increase it the catalyst slightly. The increase in ethene consumption seemed to depend on the homogeneity of the system: when the polymer was insoluble in the reaction medium the consumption increased with the comonomer addition, whereas when it was soluble the consumption began to decrease. This would suggest that also the diffusion phenomena plays a role in the rate enhancement.

The synergistic effect did not seem to be at work with the Cp_2ZrCl_2 catalyst. When the concentration of 1-butene was increased, the content of the long chain α-olefin was decreased, although the consumption of ethene decreased. Possibly the higher the 1-butene concentration is, the more there are [R-(1-butene)-cat] active centers, which favor the addition of ethene and 1-butene rather than 1-octadecene.

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