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Observations on the Rate Enhancement Effect with $MgCl_2/TiCl_4$ and Cp_2ZrCl_2 Catalyst Systems upon 1-Hexene Addition

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ABSTRACT: Ethene was copolymerized with 1-hexene in the presence of heterogeneous $MgCl_2/TiCl_4$ and homogeneous Cp_2ZrCl_2 catalysts to study the effect of 1-hexene addition on the ethene polymerization system. With both catalyst systems, 1-hexene had a rate-increasing effect. Compared with homopolymerization, the ethene consumption was increased as much as 8-fold with $MgCl_2/TiCl_4$ and 2.5-fold with Cp_2ZrCl_2. With Cp_2ZrCl_2 catalyst rate enhancement was apparent only when the polyethene was insoluble in the reaction medium. At higher temperatures, where the product was soluble, there was no rate enhancement but rather a rate decrease.

Introduction

In Ziegler–Natta catalysis, the rate enhancement effect seen as increased ethene consumption upon comonomer addition is well known, but the reason for it is uncertain. Several explanations, both chemical and physical, have been proposed, including modification of the catalytic sites with increase in the number of active centers,[1–6] diffusion,[7,8] or both of these but with the former dominating.[9,12] Related to this, we have reported a "synergistic effect" in which a short-chain comonomer increases the reactivity of a higher α-olefin.[13–15] The reason for this is probably the same as for the rate enhancement effect and will be discussed in another report.

The phenomenon discussed here has been widely studied with titanium catalysts on a $MgCl_2$ support with or without donors but also on MgH_2[16] and various silicas.[3,11] As well, the effect has been seen with supported chromium catalysts[17] and a Solvay-type $TiCl_3/Cp_2TiMe_2$ catalyst system.[8] The added comonomers have included propene, 1-butene, 1-hexene, 1-octene, and 4-methyl-1-pentene. A polymerization rate enhancement effect has been seen not only for ethene but also for propene and 4-methyl-1-pentene.[4,18,19]

Although research on metallocene catalysts has increased dramatically in recent years, only a few studies have looked at rate enhancement in the presence of metallocene catalysts,[20–23] and in none was the ethene consumption continuously monitored. In the work reported here, the rate enhancement of ethene polymerization was investigated using both heterogeneous $MgCl_2/TiCl_4$ and homogeneous Cp_2ZrCl_2 catalysts and monitoring the ethene consumption continuously.

Experimental Section

Apparatus and Method of Polymerization. Polymerizations were performed in *n*-heptane in a 0.5-dm^3 stainless steel reactor at 60 °C and 2.5-bar ethene overpressure for $MgCl_2/TiCl_4$ catalyst and at 50 and 95 °C and 1.5-bar overpressure for Cp_2ZrCl_2 catalyst. A propeller-like stirrer, was used to stir the reaction mixture at 800 rpm.

n-Heptane (260 cm^3 for polymerizations with $MgCl_2/TiCl_4$ catalyst and 290 cm^3 for polymerizations with Cp_2ZrCl_2 catalyst) was introduced into the evacuated and N_2-purged reactor. Cocatalyst solution was pumped into the reactor at the polymerization temperature, and ethene feed was started. Consumption of ethene was followed with a mass flow controller connected to a computer with an acquisition frequency of 1 Hz. After equilibrium was reached, polymerization was initiated by pumping the Cp_2ZrCl_2 catalyst/toluene solution into the reactor. The 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 the reactor temperature was controlled with a thermostat connected to a Pt-100 resistance therometer. Comonomer, if any, was pumped into the reactor. The accuracy of the pressure control was ±0.03 bar, and the reactor temperature was controlled to ±0.1 °C.

After polymerization, the reactor was degassed, and the reaction medium was washed with diluted hydrochloric acid and water and precipitated with acetone. The product was dried in vacuo at 60 °C overnight.

Chemicals. The heterogeneous catalyst was a supported Ziegler–Natta catalyst of type $MgCl_2/TiCl_4$ without donors; the triethylaluminum was a 10 wt % solution in *n*-heptane (from

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Table I. Polymerizations with $MgCl_2/TiCl_4$ Catalyst

run	time[a] (min)	1-hexene added (mol)	yield (g)	crystallinity (%)	T_m(peak) (°C)	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A1			4.2	50	136.7	nd	nd
B1	0	0.09	21.8	36	123.2	411	10.8
C1	8	0.09	5.1	37	125.8	382	7.6
D1	15	0.09	6.8	34	126.9	445	9.6
E1	30	0.09	6.9	38	128.2	497	8.8
F1	15	0.22	9.6	20	123.4	280	13.9
G1	30	0.22	9.1	35	127.5	330	10.6

[a] Time from the beginning of the polymerization when 1-hexene was added.

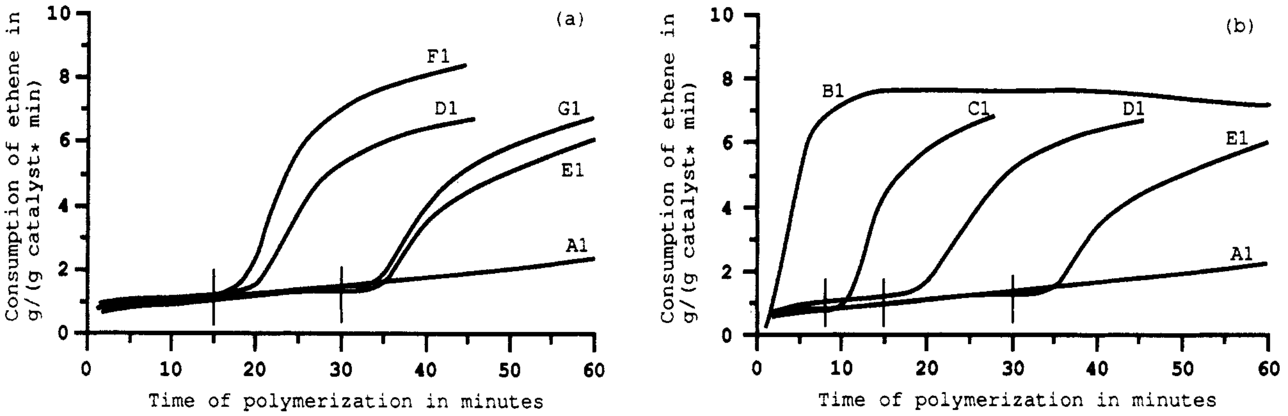

Figure 1. Dependence of the ethene consumption on the length of the homopolymerization and the amount of 1-hexene added: $MgCl_2/TiCl_4$ catalyst. Homopolymerization (A1); 0.09 mol of 1-hexene added at the beginning of the polymerization (B1), after 8-min homopolymerization (C1), after 15-min homopolymerization (D1), and after 30-min homopolymerization (E1); 0.22 mol of 1-hexene added after 15-min homopolymerization (F1) and after 30-min homopolymerization (G1); $t = 60$ °C, $p(C_2H_4) = 2.5$ bar, triethylaluminum = 4.5 mmol, Ti = 0.042–0.047 mmol.

Table II. Polymerizations with Cp_2ZrCl_2 Catalyst

run	time[b] (min)	1-hexene added (mol)	yield (g)	crystallinity (%)	T_m(peak) (°C)	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A2			17.2	53	135.3	255	3.3
B2	0	0.1	38.4	40	112.0	28	2.8
C2	8	0.1	27.5	41	111.3 and 128.0	46	5.1
D2	15	0.1	23.7	47	109.6 and 130.7	88	11.0
E2	30	0.1	19.8	50	102.5 and 129.6	180	12.9
F2	8	0.27	35.9	18	89.2 and 128.7	27	9.0
G2	15 and 42	0.27 and 0.1	33.3	24	89.5 and 130.2	40	13.3
H2[a]			5.4	66	135.6	16	3.2
I2[a]	0	0.1	6.2	37	108.0 and 123.4	4	4.4
J2[a]	15	0.1	5.8	59	104.8 and 129.4	11	5.5
K2[a]	15	0.1[c]	7.0	36	129.0	15	3.7
L2[a]	15	0.03[d]	6.4	66	112.8 and 129.8	14	2.8

[a] Polymerization temperature 95 °C, elsewhere 50 °C. [b] Time from the beginning of the polymerization when comonomer was added. [c] Comonomer 1-octadecene. [d] Comonomer 1-octene.

Schering AG). The metallocene catalyst was from Aldrich-Chemie, and methylaluminoxane, from Schering AG, was 10 wt % in toluene.

n-Heptane was grade GR from J. T. Baker, ethylene was grade 2.7 from AGA, and 1-hexene, 1-octene, and 1-octadecene were from Aldrich-Chemie. All of these reagents were further purified by passing them through columns containing CuO and Al_2O_3 molecular sieves.[24]

Polymer Characterization. DSC curves were obtained from powder form (4.5 ± 0.2 mg) samples. The starting temperature was 0 °C, the heating rate was 10 °C/min, and the end temperature was 180 °C. Samples were heated twice and between the runs they 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 the heat of fusion.

Molar masses were investigated with a Waters high-temperature GPC device equipped with three TOSOH mixed-bed columns with an exclusion limit for polystyrene of 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.

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 I. As shown in Figure 1a, with $MgCl_2/TiCl_4$ catalyst and 0.1 mol of 1-hexene added at the beginning of the polymerization, the ethene consumption increased 8-fold relative to the homopolymerization rate and the maximum was reached very rapidly (B1). When 1-hexene was added to the reactor after 30 min of homopolymerization of ethene, the consumption increased much more slowly (E1). Evidently, the longer the homopolymerization step, the slower was the increase in the consumption of ethene, although ethene homopolymerization (A1) exhibited a slight activation. This has also been reported by Calabro and Lo.[3]

Figure 1b shows that ethene consumption increased as comonomer was added. The same kind of increase was seen by Calabro and Lo[3] (1-hexene) and Vindstad et al.[12] (propene). As in Figure 1a, it is clear that the earlier the 1-hexene was added, the more rapidly the consumption increased.

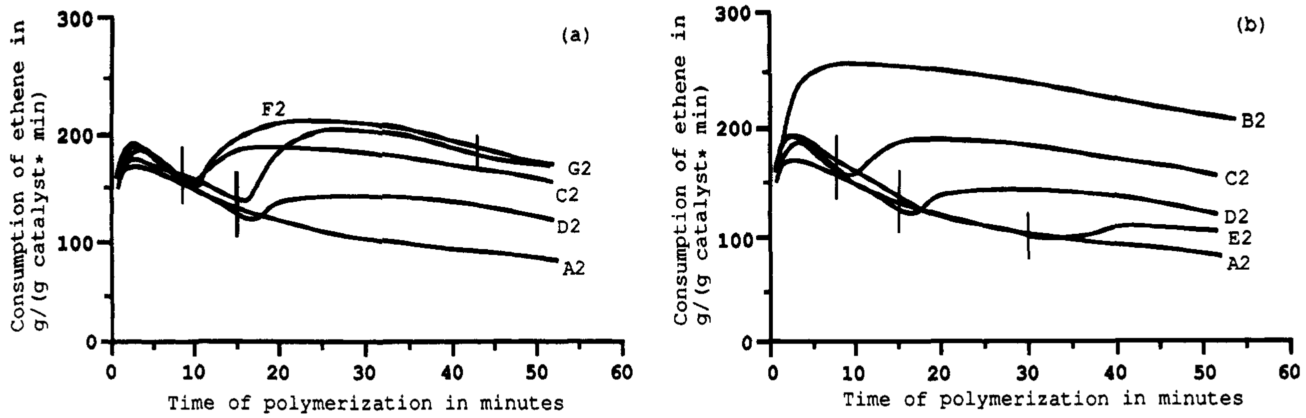

Figure 2. Dependence of the ethene consumption on the length of the homopolymerization and the amount of 1-hexene added: Cp_2ZrCl_2 catalyst. Homopolymerization (A2); 0.1 mol of 1-hexene added at the beginning of the polymerization (B2), after 8-min homopolymerization (C2), after 15-min homopolymerization (D2), and after 30-min homopolymerization (E2); 0.27 mol of 1-hexene added after 8-min homopolymerization (F2); 0.27 and 0.1 mol of 1-hexene added after 15-min homopolymerization and after 27-min copolymerization, respectively (G2); t = 50 °C, $p(C_2H_4)$ = 1.5 bar, Al = 9.7 mmol (as methylaluminoxane), Zr = 10.3 × 10^{-3} mmol.

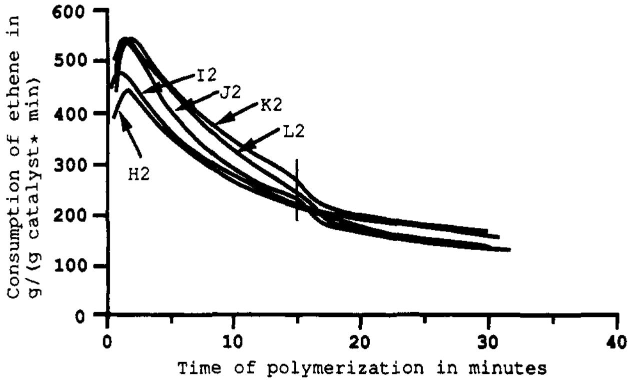

Figure 3. Dependence of the ethene consumption on the length of the homopolymerization and the amount of 1-hexene added: Cp_2ZrCl_2 catalyst. Homopolymerization (H2); 0.1 mol of 1-hexene added at the beginning of the polymerization (I2) and after 15-min homopolymerization (J2); 0.1 mol of 1-octadecene added after 15-min homopolymerization (K2); 0.1 mol of 1-octene added after 15-min homopolymerization (L2); t = 95 °C, $p(C_2H_4)$ = 1.5 bar, Al = 9.7 mmol (as methylaluminoxane), Zr = 2.4 × 10^{-3} mmol.

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 II. When the polymerization temperature was 50 °C, the polyethene obtained did not dissolve in n-heptane. Thus this cannot be considered as a true homogeneous case.

The rate enhancement seen with $MgCl_2/TiCl_4$ catalyst was also clearly observed with Cp_2ZrCl_2 catalyst (Figure 2a). However, the increase was smaller than with the titanium catalyst, at most only 2.5 times the homopolymerization rate. Once again, as with the titanium catalyst, the longer the homopolymerization step, the smaller was the consumption increase and the more slowly it occurred. When 0.27 mol of 1-hexene was added instead of 0.1 mol, the consumption increased more rapidly to the higher level (Figure 2b). In run G2 in Figure 2b, comonomer was added to the reactor twice: first 15 min after polymerization began and then again after 42 min. In the first phase when 0.27 mol of 1-hexene was added, the consumption increased very rapidly; later when 0.1 mol was added, the increase could hardly by seen.

The situation changed totally when the temperature was raised and polyethene dissolved in the reaction medium. The solubility of the polymer was checked visually when the reactor was opened. Figure 3 shows the three polymerizations performed at 95 °C. When 1-hexene was added during the polymerization (J2), there seemed to be a slight negative effect; in other words, addition of comonomer decreased the ethene consumption. This phenomenon was further checked with 1-octene and 1-octadecene (L2 and K2, respectively). 1-Hexene was also added at the beginning of the polymerization (H2), but here it is difficult to say if the addition increased or decreased the ethene consumption.

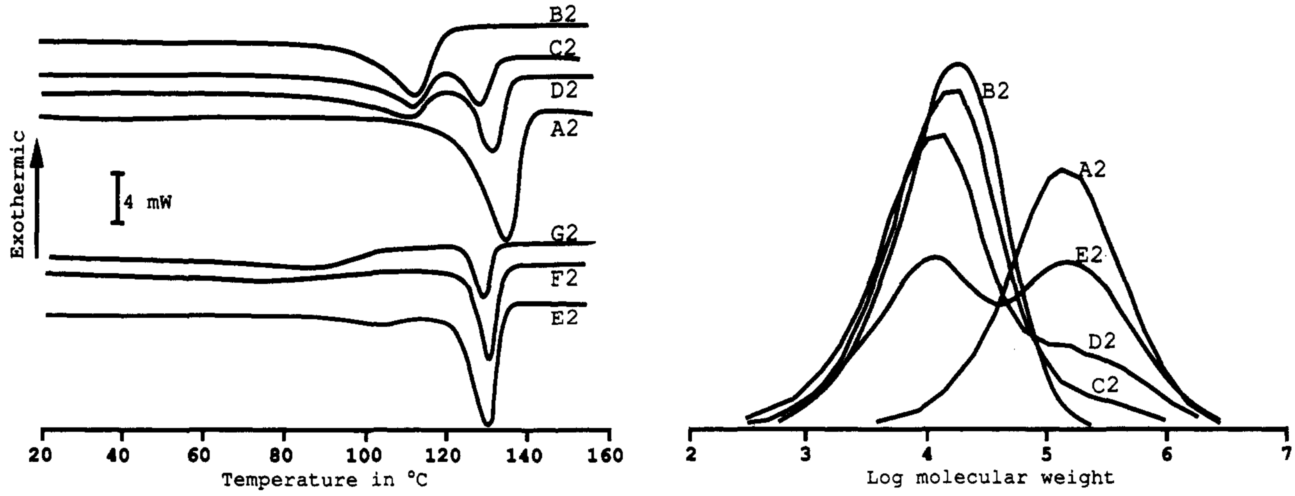

Figure 4. Differential scanning calorimetry runs and molar mass distributions of selected samples obtained with Cp_2ZrCl_2 catalyst. Homopolymerization (A2); 0.1 mol of 1-hexene added at the beginning of the polymerization (B2), after 8-min homopolymerization (C2), after 15-min homopolymerization (D2), and after 30-min homopolymerization (E2).

In a good solvent all the zirconium atoms are said to be active.[21] So here it can be assumed that no more inactive catalyst centers were available and the addition of comonomer did not increase the ethene consumption. A double check of these three runs gave the same result, a result Chien and Nozaki[23] call the negative comonomer effect. They believe it to arise from a competition between ethene and 1-hexene in π-complexation with the metallocene.

Figure 4 displays the molar mass distributions and differential scanning calorimetry runs of selected samples made with Cp_2ZrCl_2 catalyst. As can be seen, the molar mass decreased remarkably upon comonomer addition, and the molar mass distribution became bimodal when the comonomer was added after polymerization had begun. The peak rising in the high molar mass area represents the homopolymer part of the polymer, and the peak in the lower molar mass area represents the copolymer part. As seen in Table I, molar mass decrease was also seen with the $MgCl_2/TiCl_4$ catalyst. The same pattern seen in the GPC curves is reproduced in the DSC curves: two melting peaks appeared when comonomer was added during the polymerization (Figure 4).

As can be seen in Tables I and II, the crystallinity of the polymer decreases when comonomer is incorporated into the polymer chain. One reason for the double peaks might be that the comonomer here acts as a chain transfer agent, lowering the molar mass. Or possibly the comonomer modifies the catalyst center so that it produces low molar mass, low-melting polymer, and the modified centers polymerize more ethene than the unmodifier centers.

Monomer diffusion is said to play an important role in the polymerization of ethene both with highly active metallocene catalyst[25] and with supported titanium catalyst.[26] Decrease in the crystallinity and in the molar mass of the polymer both make the polymer more soluble in the reaction medium so perhaps the monomer diffusion rate in the polymer increases at the same time. Supporting this idea are the slower increase in ethene consumption the later the comonomer is added and the more agglomerated and larger diameter polyethene particles. On the other hand, Tait et al.[9,10] and Pasquet and Spitz[6] have shown that the addition of comonomer increases the amount of active sites and that active centers are dying and born all the time, so the rate enhancement cannot be explained by the diffusion alone.

Calabro and Lo[3] explained the rate enhancement not by mass transfer limitations but by comonomer participating in the catalyst activation. Relevant to this, it may be that as the solubility of the polymer increases, the agglomeration of the growing particles is hindered and the number of easily accessible catalytic sites are increased. As we have seen, the rate enhancement effect disappeared once the polymer was totally dissolved.

Conclusions

Here an examination of the rate enhancement effect both with a heterogeneous $MgCl_2/TiCl_4$ catalyst and with a homogeneous Cp_2ZrCl_2 catalyst was made. The effect was seen with both of these catalyst systems; however, with the zirconium catalyst, the effect was seen only when the polymer formed was insoluble in the reaction medium. The comonomer addition makes the formed polymer more soluble and so perhaps the number of easily accessible catalytic centers are increased.

When the polymer was soluble in the reaction medium, a negative comonomer effect was seen. In this case, no growing and agglomerating polymer particles and no mass transfer limitations are present. Moreover, it can be assumed that every zirconium atom is active. In this case it is reasonable that the addition of comonomer does not increase the ethene consumption.

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