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Low Molecular Weight Ethylene/Propylene Copolymers. Effect of Process Parameters on Copolymerization with Homogeneous Cp_2ZrCl_2 Catalyst

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ABSTRACT: In ethylene/propylene copolymerizations with cyclopentadienylzirconium dichloride (Cp_2ZrCl_2)/methylaluminoxane (MAO) catalyst, correlations were found between polymerization temperature (−15 °C to +55 °C), catalyst activity, and viscosity average molecular weight. As the polymerization temperature increased, the activity of the catalyst increased and the viscosity average molecular weight of the copolymer product decreased. The activity of the catalyst was higher than that reported earlier, even with the differences in polymerization conditions taken into account. Changing the solvent from heptane to toluene had no effect on the viscosity average molecular weight of the product. In toluene the catalyst activity was higher. The higher the amount of propylene in the feed, the lower the viscosity average molecular weight. Increase in the catalyst mole ratio from 2300 to 6900 Al/Zr did not affect either the catalyst activity or the viscosity average molecular weight of the copolymer. As expected for metallocene catalyst, GPC analysis showed the molecular weight distribution of the products to be narrow.

Introduction

A homogeneous metallocene/methylaluminoxane (MAO) catalyst system is superior to heterogeneous catalysts and homogeneous vanadine catalyst for ethylene/propylene copolymerizations.[1-21] Product properties can be varied by changing the polymerization temperature or the comonomer concentration. Copolymers with propylene concentrations ranging from 10 to 90 wt % have been produced.[5,6,23]

Zirconium catalysts are more active in ethylene polymerizations and copolymerizations than the analogous titanium and hafnium catalysts,[1,8,9,22] and as a cocatalyst, MAO is more effective than ethyl- or isobutylaluminoxane. Bis(cyclopentadienyl) compounds containing chlorine ligands possess higher activities than do "chlorine-free" systems, especially at low polymerization temperatures.[6] Owing to the special properties of metallocene catalysts, the molecular weight distributions obtained with them are very narrow and thus clearly different from those obtained with conventional Ziegler–Natta catalysts.[24]

At the moment there is no clear understanding of the relation between polymerization conditions and polymer structure. In this work we studied how process parameters in copolymerization of ethylene and propylene with the homogeneous metallocene catalyst Cp_2ZrCl_2 influence the polymer properties. The process parameters investigated were temperature, Al/Zr molar ratio, and solvent, and the effects of interest were catalyst activity and polymer molecular weight or intrinsic viscosity. Crystallinity and molecular weight distribution of samples were also determined.

Experimental Section

Apparatus and Polymerization Method. Copolymerizations were performed in *n*-heptane or toluene in a 0.5-dm^3 stainless steel reactor. In the semiflow method employed, monomers were fed through the reactor continuously. No hydrogen was used. Part of each monomer was polymerized and the rest discharged. If the conversion of the monomers was low, the monomer composition in the reaction medium remained constant.

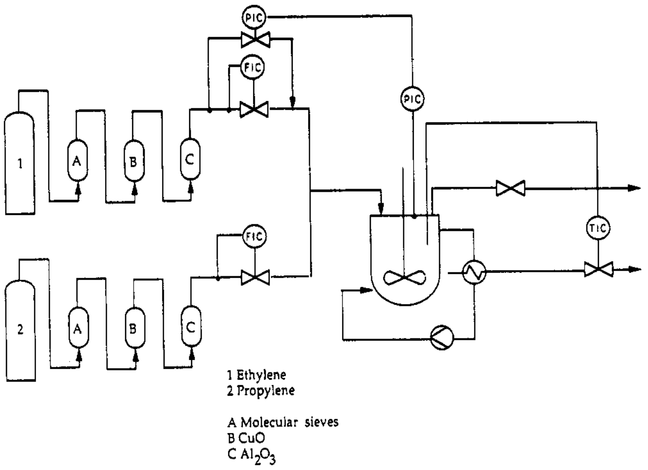

Figure 1. Flow sheet of the reactor system used in ethylene/propylene copolymerization.

Polymerization time was 45 min and total pressure applied was 1.5 bar. The amount of metallocene added was 2.0 mg. The catalyst was dissolved in toluene and the solution was placed in small ampules, which were capped to provide protection from light, oxygen, and air moisture. The concentrations of ethylene and propylene were kept constant during the polymerization. A flowsheet of the reactor system is presented in Figure 1. More detailed information of the reactor system can be found in some earlier papers of our group.[24,25]

Heptane was fed to the reactor through fixed lines and heated or cooled depending on the desired polymerization temperature. Feeding of monomers was then begun; the cocatalyst was injected into the reactor and then the catalyst solution. Pressure was regulated to the desired level. When polymerizing in toluene, this was fed to the reactor through a funnel and bubbled with nitrogen about 45 min before sealing of the reactor and starting the temperature regulation and monomer feed.

At the end ethylene and propylene feed was stopped and the reactor was degassed. The polymer solution was washed with diluted hydrochloric acid and water and precipitated with acetone. The product was dried in vacuum at 60 °C overnight.

The pressure inside the reactor was maintained constant manually by regulating a needle valve in the gas outlet line. Reactor temperature was controlled automatically with a Lauda R400 thermostat connected to a Pt-100 thermocouple. Temperatures below 20 °C were controlled manually by circulating

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a water–ethanol mixture in the jacket of the reactor. Accuracies of pressure and temperature control were ±0.3 bar and ±0.5 °C, respectively.

Chemicals. The catalyst was the soluble metallocene catalyst bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) from Witco and the cocatalyst was 10 wt % methylaluminoxane (MAO) in toluene from Schering. The Al content of the cocatalyst was 4.5–5.5 wt %.

Propylene was of grade 2.5 (from Messer-Griesheim) and ethylene of grade 2.7 (from AGA). Ethylene was further purified just before entering the reactor by conducting it through columns containing molecular sieves, CuO, and Al_2O_3. Heptane was of grade RG from JT Baker and toluene was of grade RG from Riedel-de Häen.

Polymer Characterization. One-point intrinsic viscosities were measured at 135 °C with decahydronaphthalene as solvent. The relative viscosity (η_{sp}) was determined and the intrinsic viscosity (η_{intr}) calculated according to Solomon and Ciuta.[26]

The viscosity average molecular weight of most of the samples was determined on the basis of the intrinsic viscosity measurements, and the ethylene/propylene ratio of the product was determined by IR spectroscopy. The IR spectrophotometer used was a Philips PYE UNICAM SP3-100. The determination of the ethylene of the product content was carried out according to Paroli *et al.*[27]

The viscosity average molecular weight of the sample was calculated according to Scholte *et al.*[28] Molecular weight distribution was determined with a Waters 150-C ALC/GPC instrument equipped with Shodex mixed bed columns. The solvent was 1,2,4-trichlorbenzene with a flow rate of 1.0 mL/min. A low density polyethylene standard of broad molecular weight distribution was used for universal calibration. The monomer composition of the copolymers was taken into account according to the literature.[28]

Ethylene contents and triad sequence distributions of selected products were determined with a Jeol GSX-400 ^{13}C nuclear magnetic spectrometer. Calculations were made according to Cheng.[29–31]

Crystallinities were determined with a Mettler DSC. The sample was melted twice, and the results of the second run were taken for comparison to ensure that the thermal history of the samples was similar. Temperature range used in the analysis was −100 to 250 °C. Melting and cooling were carried out at 10.0 °C/min.

Results and Discussion

Polymerization conditions, catalyst activities, and viscosity average molecular weights of the products are presented in Table 1. In experiments 1–25 the average ethylene content of the products was 60 wt %.

Al/Zr Mole Ratio. In the range of Al/Zr mole ratios studied (2300, 3400, 4500, and 6800, experiments 1–7 in Table 1) the catalyst ratio appeared to have no effect on either the catalyst activity or the viscosity average molecular weight. The exceptional values in experiments 3 and 6 are presumably due to unrelated causes.

Temperature. The effect of temperature on polymer properties was investigated between −15 and +55 °C. The higher the temperature, the higher the catalyst activity and the lower the viscosity average molecular weight (Table 1). Figure 2 shows the effect of temperature on the activity of the catalyst and Figure 3 the effect of temperature on the viscosity average molecular weight. Although it would be desirable to find a temperature at which both catalyst activity and molecular weight are at maximum, this was not possible for our catalyst since the two parameters vary in reverse directions.

The activity of the catalyst also varied with the solubility of the copolymer in the solvent. At lower temperatures (<5 °C), a bulky product was obtained, while at higher temperatures the product was almost totally dissolved in the solvent.

Table 1. Polymerization Conditions, Catalyst Activity, and Viscosity Average Molecular Weight for Copolymerizations of Ethylene and Propylene[a]

run no.	T_p (°C)	Al/Zr ratio	catal activity (kg of pol/g of cat)	$\bar{M}_v$ (g/mol)
1	40	2300	15.1	5100
2	40	2300	16.2	4100
3	40	2300	2.0	1300
4	40	3400	17.4	2000
5	40	4500	19.0	3000
6	40	4500	2.0	3200
7	40	6900	16.9	3800
8	55	2300	14.1	2500
9	55	2300	14.8	1600
10	50	2300	13.9	2600
11	25	2300	13.3	11200
12	25	2300	5.4	13500
13	15	2300	0.3	28100
14	5	2300	5.4	58500
15	0	2300	5.9	83500
16	−5	2300	5.4	99200
17	−10	2300	7.7	81800
18	−10	2300	2.5	80800
19	−10	2300	1.4	75800
20	−15	2300	2.5	130800
21	−15	2300	1.3	96300
22[b]	40	2300	15.6	7400
23[b]	55	2300	21.5	<100
24[b]	25	2300	10.7	5700
25[b]	0	2300	1.0	86100
26[c]	40	2300	14.4	10900
27[c]	40	2300	16.3	7800
28[c]	40	2300	5.1	300

[a] Soluble metallocene catalyst Cp_2ZrCl_2 2.0 mg, total pressure 2.5 bar, solvent 290 cm^3. [b] Toluene used as solvent. [c] Ethylene to propylene ratio in feed 2:1. [d] Ethylene to propylene ratio in feed 1:2.

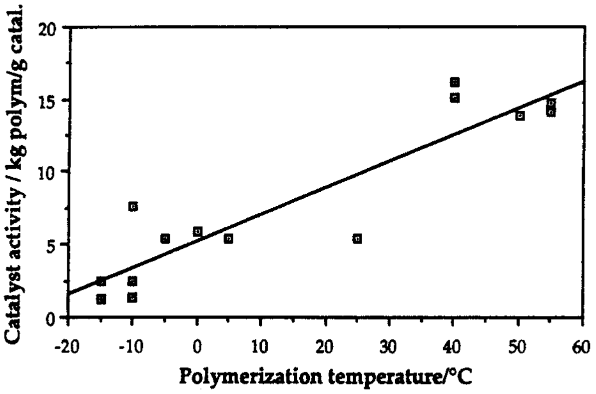

Figure 2. Effect of temperature on the activity of the catalyst. Polymerizations were carried out in 290 cm^3 of heptane: Al/Zr molar ratio 2300; amount of catalyst 2.0 mg; pressure 2.5 bar; polymerization time 45 min.

The intrinsic viscosity was low in all cases. The lowest intrinsic viscosity corresponded to a viscosity average molecular weight of about 1300 g/mol and the highest to about 138 000 g/mol. The polymers prepared at temperatures above 25 °C were waxlike. As the molecular weight grew when the temperature was decreased, the product became more like solid thermoplastic polymer.

Figure 4 shows the strong dependence of the molecular weight distribution (MWD) on temperature. Narrow distributions are typical for metallocene catalysts.

Polydispersity increased slightly with temperature and ranged from 1.5 to 2.8 in these experiments—a typical range for metallocene catalysts. Likewise the very narrow MWDs are typical for metallocene catalysts and indicate that there is one dominant type of catalytic sepcis in the system.

Change in the polymerization temperature appeared to have no significant influence on the ethylene content of

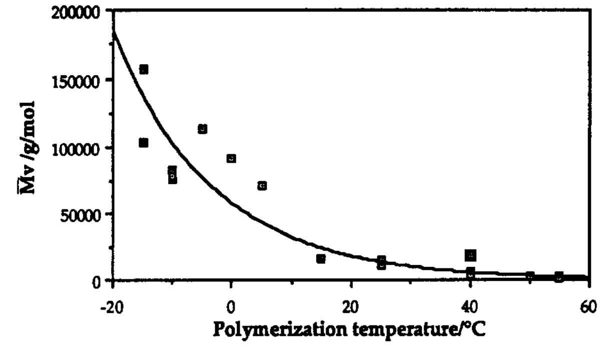

Figure 3. Effect of polymerization temperature on viscosity average molecular weight of the copolymer. Polymerizations were carried out in 290 cm^3 of heptane: Al/Zr molar ratio 2300; amount of catalyst 2.0 mg; pressure 2.5 bar; polymerization time 45 min.

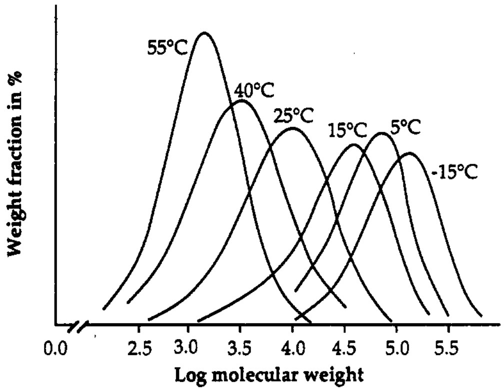

Figure 4. Molecular weight distribution plots for ethylene/propylene copolymers produced at different temperatures. The polymerizations were carried out at 40 °C in 290 cm^3 of heptane: Al/Zr molar ratio 2300; amount of catalyst 2.0 mg; pressure 2.5 bar; polymerization time 45 min.

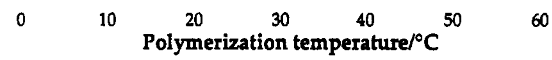

Figure 5. Effect of temperature and solvent on viscosity average molecular weight of the copolymer. Polymerizations were carried out in 290 cm^3 of heptane and toluene: Al/Zr molar ratio 2300; amount of catalyst 2.0 mg; pressure 2.5 bar; polymerization time 45 min.

the polymer, indicating that the reactivity ratios of the monomers do not change in the temperature range studied.

Effect of the Solvent. To study the effect of the solvent on the polymerization, several polymerizations were carried out in 290 cm^3 toluene. Although the product dissolved better in toluene than in heptane, the activity of the catalyst and the viscosity average molecular weight depended on temperature in the same way in toluene as in heptane. Also there was no significant difference in the intrinsic viscosities (and so the viscosity average molecular weights) of the products obtained in the two solvents. The results can be seen in Figure 5.

Ethylene/Propylene Ratios in the Feed. In addition to the polymerizations carried out with a 1:1 ratio of ethylene to propylene, three trials were made with the monomer ratios 1:2 and 2:1. As shown in Table 2, intrinsic viscosities and viscosity average molecular weights were increased at the higher ratio of ethylene to propylene. Nonbridged bis(indenyl)zirconium catalyst behaves differently[14] producing copolymers whose molecular weight decreases with the increase of ethylene in the feed.

Table 2. Dependence of the Intrinsic Viscosity of the Copolymer on Ethylene/Propylene Ratio in the Feed[a]

run no.	ethylene to propylene ratio	η (dL/g)	$\bar{M}_v$ (g/mol)
2	1:1	0.15	4100
26	2:1	0.33	10900
27	2:1	0.26	7800
28	1:2	0.02	300

[a] Polymerizations were carried out at 40 °C in 290 cm^3 of heptane: Al/Zr molar ratio 2300; amount of catalyst 2.0 mg; pressure 2.5 bar; polymerization time 45 min.

Crystallinity and Glass Transition Temperature. Crystallinity and glass transition temperature of the samples were determined by DSC. The many melting peaks in the curves indicate that there were many kinds of structures in the copolymer. The broad melting peak in the range 0–50 °C is typical of crystalline rubbers where ethylene content exceeds 50 wt %.

Copolymers were either amorphous or contained very little crystallinity: measured crystallinities ranged from 0 to 0.16%. Temperature had little if any effect on the crystallinity of the product. Because of the several broad melting peaks, no clear dependencies could be found between the glass transition temperature and processing temperature.

Discussion. Although the activity of Cp_2ZrCl_2 is reported[14] to be lower than that of $Et[Ind]_2ZrCl_2$, we found it to be more or less the same. However, the amount of catalyst and the Al/Zr mole ratio used were half of the values in the earlier work.[14] Taking the differences in polymerization conditions into account, the catalyst activities in our work were at the level achieved by Chien and Xu[32] with zirconocenium ion, which is an exceedingly active catalyst. The temperature dependence of the catalyst activity was nevertheless stronger in our study than it was in that of Chien and Xu.[32]

The viscosity average molecular weight was low for all the copolymers studied. The activity of the catalyst was 19 kg of polymer/(g of catalyst bar h) for the copolymer having viscosity average molecular weight 2500 g/mol. The highest molecular weight was 157 000 g/mol, which was obtained at −15 °C. The intrinsic viscosities obtained in toluene were somewhat lower than those reported by Kaminsky and Schobom[12] using catalyst $Cp_2Zr(CH_3)_2$, but the polymerization conditions were not quite the same in their study as in ours. Changing the solvent from heptane to toluene did not affect the molecular weight but only the catalyst activity, which was better in toluene. The molecular weight distribution was narrow, as is typical for metallocene catalysts.

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