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Combined metallocene catalysts: an efficient technique to manipulate long-chain branching frequency of polyethylene

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SUMMARY: The solution polymerization of ethylene in Isopar E in a semi-batch reactor using combined CGC-Ti and Et[Ind]$_2$ZrCl$_2$ catalysts was studied. Methylaluminoxane (MAO) and tris(pentafluorophenyl)borane were used as co-catalysts. Samples were analyzed by ^{13}C NMR and gel permeation chromatography (GPC) for their branching content and molecular weight distribution. It was shown that there was an optimum ratio of CGC-Ti/Et[Ind]$_2$ZrCl$_2$ that maximizes the number of long-chain branches of the formed polyethylene.

Introduction

Lai et al.[1,2] were the first to describe the production of polyethylenes with long-chain branches using metallocene catalysts. They employed a monocyclopentadienyl metallocene catalyst (constrained geometry catalyst) to incorporate macromonomers, formed in-situ, into the polymer backbone and synthesized polyethylenes with long-chain branches. These macromonomers are dead polymer chains with terminal double bonds formed via β-hydride elimination reaction.

Soares and Hamielec[3,4] developed a mathematical model for homo- and copolymerization of ethylene and α-olefins that takes into account long-chain branch formation using metallocene catalysts. They obtained an analytical solution for the chain length and chemical composition distributions of the populations containing different number of long chain branches per molecule for a CSTR (continuous stirred tank reactor) operating at steady state.

Beigzadeh et al.[5,6] expanded the kinetic model proposed by Soares and Hamielec[3,4] for homo- and copolymerization of ethylene and α-olefins using a combined metallocene catalyst. They investigated the effect of different process conditions and characteristics of the combined catalyst on the microstructure of the polymer made in a CSTR operating dynamically and at steady-state. They showed that by combining CGC-Ti with a second metallocene catalyst (with higher β-hydride elimination rate constant than CGC-Ti) to the polymerization system of Lai et al.[1,2], long-chain branching could be increased. Their modeling results suggested that by changing the type and the amount of the second metallocene catalyst, long-chain branching could be manipulated.

The present work investigates the validity of some of the modeling results obtained by Beigzadeh et al.[5,6] In this work polymerization of ethylene using a combined catalyst in a semi-batch reactor was studied. The effect of the ratio of the two catalysts on LCB (long-chain branching) degree and MWD is the main focus of this study. The synthesized polymer samples were analyzed with ^{13}C NMR and GPC for their long-chain branching frequencies and molecular weight distributions (MWD), respectively.

Experimental part

Materials

Isopar E (2,2,4-trimethylpentane), donated by Exxon Chemical Co., was purified by contacting with molecular sieves under nitrogen bubbling for at least 12 h in order to remove moisture and oxygen.

Titanium (*N*-1, 1-dimethylethyl)dimethyl (1-(1,2,3,4,5-η)-2,3,4,5-tetramethyl-2,4-cyclopentadiene-1-yl)silanaminato)) (2-)*N*)-dimethyl (1% solution in Isopar E), from now on called CGC-Ti, was donated by Dow Chemical Co. Dichloro[*rac*-ethylenebis(indenyl)]zirconium(IV) was purchased from Aldrich Chemical Co.

Methylaluminoxane (MAO-30% solution in toluene) was purchased from Albemarle Corporation. Tris(pentafluorophenyl)borane (TPFB) was donated by Dow Chemical Co. (3.58% solution in Isopar E).

Polymerization

Polymerization of ethylene was carried out in a 600 cm^3 autoclave reactor. The reactor was equipped with a mechanical stirrer, an electrical heating element, and a cooling coil. Measured amounts of TPFB ([TPFB]/[Catalyst] = 100), MAO ([Al]/[Catalyst] = 500), and hydrogen (0–20 ml; 0–0.9 mmol) were added to the reactor containing 400 cm^3 of Isopar E as the solvent. The reactor was heated up to the reaction temperature and pressurized with ethylene until the solvent was saturated. Polymerization started by injecting the catalysts into the reactor. The overall amount of catalyst in the reactor was kept 1.6 μmol for all runs, but the ratio CGC-Ti/(CGC-Ti + Et[Ind]$_2$ZrCl$_2$) was varied from 0 to 1.0.

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All of the polymerization runs were conducted at 140 °C and 1792 kPa (260 psi) for 10 min and terminated by injecting acidic ethanol. Approximately 0.4 mol of ethylene was fed into the reactor before the polymerization started. The precipitated polymer was adequately washed with ethanol and dried in vacuum at 60 °C for 10 h.

Characterization

Gel permeation chromatography (GPC) was used to determine the MWD of the samples. GPC analysis were performed on a high temperature Waters 150CV Plus™ instrument equipped with three Waters Styragel HT6E columns, using differential refractive index and viscometer (single capillary) detectors. About 0.2 mg of polymer sample was dissolved in 1,2,4-trichlorobenzene (TCB) as solvent. All GPC runs were carried out at 140 °C and the flow rate of 1.0 ml/min. A universal calibration method[7] with narrow polystyrene standards was used.

^{13}C NMR was used to measure the long-chain branching content of the samples. The samples were dissolved in TCB in a 10 mm diameter tube (approximately 35 wt.-% of polymer in solution). The polymer was dissolved at 150 °C for 30 min before being analyzed at 125 °C on a Bruker AC-300 NMR spectrometer. The inverse gate decoupling method was used to decouple protons from carbon nuclei. The number of scans performed for each spectrum was around 10000. Peak assignments and the long chain branch frequency calculations were done according to the methodology proposed by Randall[8, 9]. The required peak assignments are shown in Fig. 1.

Results and discussion

Based on the simulation results obtained by Beigzadeh et al.[5, 6], to increase long-chain branching the second metallocene catalyst used in the combined catalyst must be able to generate more macromonomers (dead chains with terminal double bonds) than CGC. ^{13}C NMR analysis of polyethylene samples synthesized with CGC-Ti and Et[Ind]$_2$ZrCl$_2$ individually showed that the concentration of terminal double bonds in polymer sample made with Et[Ind]$_2$ZrCl$_2$ was more than twice as much as that found for the sample made with CGC-Ti (Tab. 1). Therefore, Et[Ind]$_2$ZrCl$_2$ was used as the CGC-Ti partner in the combined catalyst. Fig. 2 illustrates how the number of long-chain branches per 10000 carbon atoms depends on the fraction of CGC-Ti in the binary mixture. Three different hydrogen levels have been studied (replicate runs for H_2 = 10 ml). As shown in this figure, by increasing the mole fraction of CGC-Ti, the plot of branching degree versus CGC-Ti mole fraction passes through a maximum. No branching was observed when only Et[Ind]$_2$ZrCl$_2$ was used. As more CGC-Ti was employed in the binary catalyst system (CGC-Ti% = 0.2, 0.35, and 0.5) the measured LCB frequencies increased up to a maximum corresponding to CGC-Ti% = 0.5. By increasing the mole fraction of CGC-Ti to more than 50%, the branching content started decreasing (CGC-Ti% = 0.65 and 0.8) to the LCB content obtained when only CGC-Ti was used. As proposed by Beigzadeh et al.[5, 6], this behavior can be attributed to a

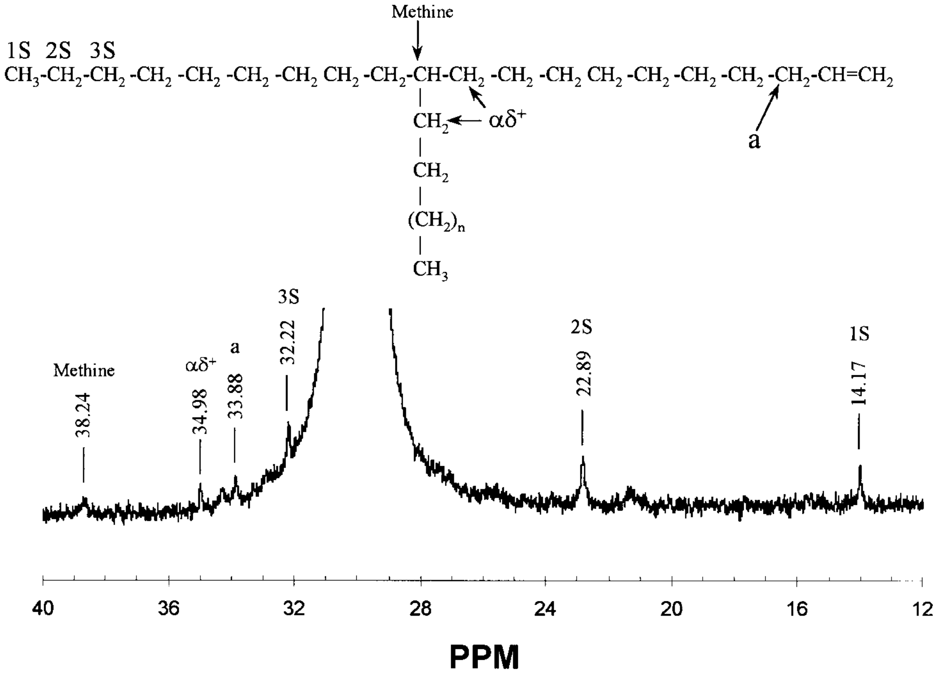

Fig. 1. Typical ^{13}C NMR spectrum with the required peak assignments for different chain structures

Tab. 1. Summary of ^{13}C NMR results and calculated LCB degrees for polyethylene samples synthesized by combined and individual CGC-Ti/Et[Ind]$_2$ZrCl$_2$. H$_2$ = 0 ml

No.	Content of CGC-Ti in mol-%	NMR Data (area under the peak)			Unsaturated/ saturated chain ends	Total carbon intensity	Br. per 10000 C[a]
		$\alpha\delta^+$ carbon	average of 1S, 2S, and 3S	allylic carbon (a)			
1	0	0	9.84	9.65	0.98	9899	0
2	20	4.42	8.16	7.34	0.90	9833	1.50
3	35	6.33	7.8	6.32	0.81	9716	2.17
4	50	12.41	7.02	5.33	0.76	9815	4.21
5	65	5.24	7.08	4.67	0.66	9757	1.79
6	80	6.81	5.75	3.1	0.54	9736	2.33
7	100	2.92	5.31	2.23	0.42	9724	1.00

[a] Branch per 10000 C = (1/3)$\alpha\delta^+$/Total carbon intensity ×10^4.

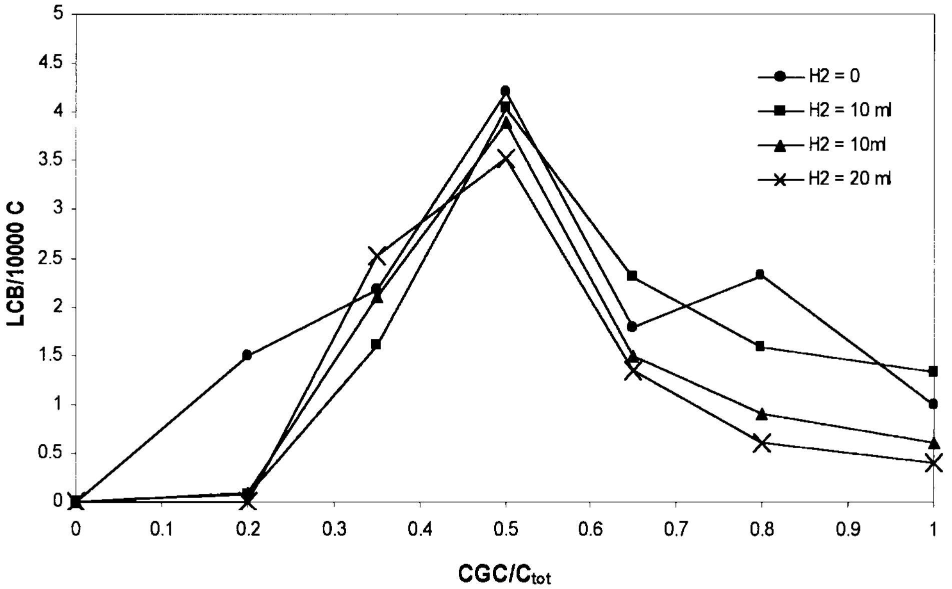

Fig. 2. Variation of LCB degree with CGC-Ti/Et[Ind]$_2$ZrCl$_2$ ratio

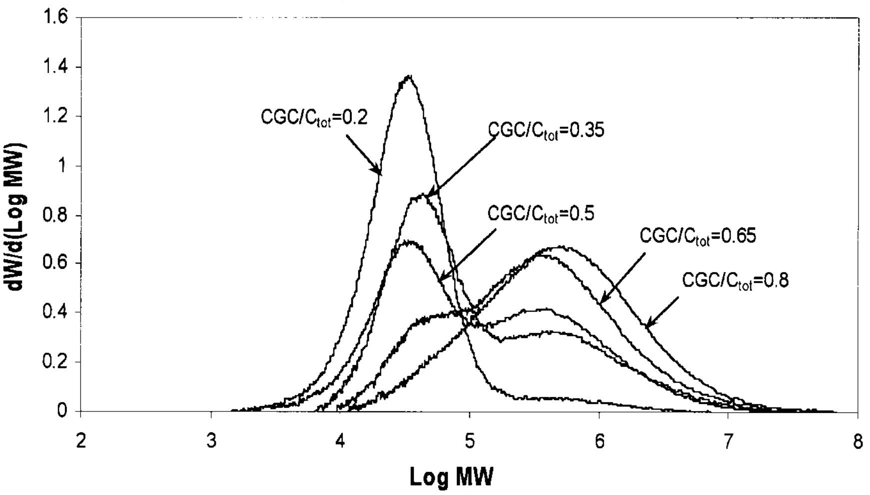

Fig. 3. Molecular weight distribution of polyethylene samples synthesized with combined CGC-Ti/Et[Ind]$_2$ZrCl$_2$. H$_2$ = 0 ml

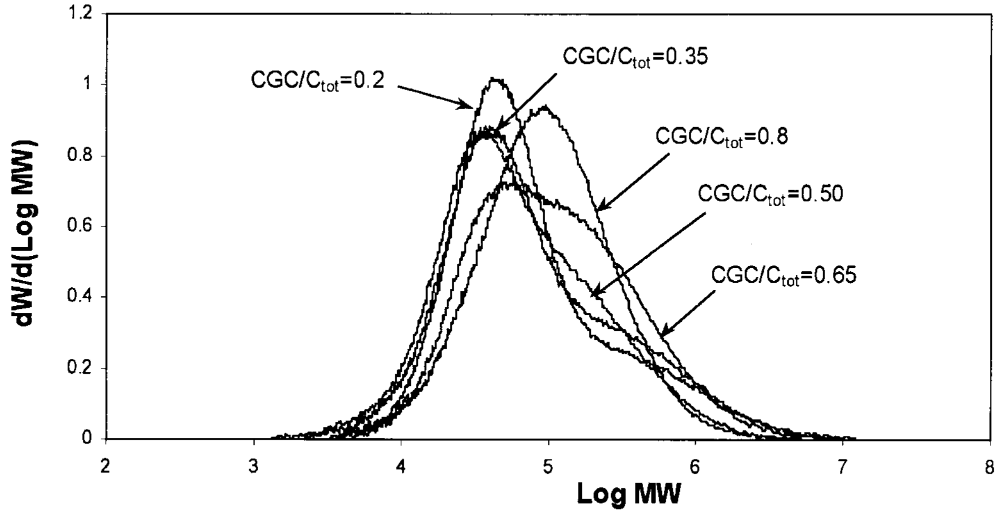

Fig. 4. Molecular weight distribution of polyethylene samples synthesized with combined CGC-Ti/Et[Ind]$_2$ZrCl$_2$. $H_2 = 10$ ml

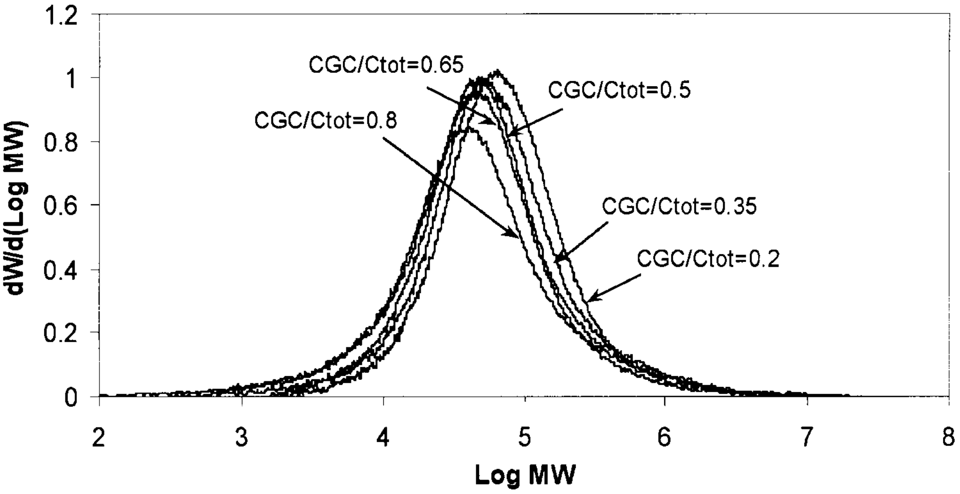

Fig. 5. Molecular weight distribution of polyethylene samples synthesized with combined CGC-Ti/Et[Ind]$_2$ZrCl$_2$. $H_2 = 20$ ml

lower macromonomer concentration as the mole fraction of Et[Ind]$_2$ZrCl$_2$ decreases. Fig. 2 also indicates that the observed optimum value for CGC-Ti mole fraction is independent of the amount hydrogen. This is also in agreement with the simulation results obtained by Beigzadeh et al.[5,6]

Fig. 3 shows the MWD of polyethylene samples synthesized with the CGC-Ti/Et[Ind]$_2$ZrCl$_2$ catalyst system. By increasing the fraction of CGC-Ti in the catalyst mixture, the high molecular weight peak of the bimodal MWD becomes larger, suggesting that the chains synthesized with CGC-Ti have higher molecular weights than the chains made with Et[Ind]$_2$ZrCl$_2$. The effect of hydrogen (chain transfer agent) on MWD is illustrated in Fig. 4 and 5. By adding hydrogen, the peak corresponding to the chains synthesized with CGC-Ti moves towards lower molecular weights, while the peak corresponding to the Et[Ind]$_2$ZrCl$_2$-made polymer chains does not shift as much. Similar observations were made by Kim et al.[10,11] for slurry polymerization of ethylene with Et[Ind]$_2$ZrCl$_2$.

Conclusion

Homopolymerization of ethylene using CGC-Ti/Et[Ind]$_2$-ZrCl$_2$ catalyst mixture was studied. It was observed that long-chain branching could be controlled by varying the ratio of the two catalysts in the reactor. For a given set of polymerization conditions and catalyst combination, there exist an optimum ratio that maximizes the number of long-chain branches of the produced polyethylene. These results are in close agreement with the previous simulation results published by Beigzadeh et al.[5,6]

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