Production of Polyolefins with Controlled Long Chain Branching and Molecular Weight Distributions Using Mixed Metallocene Catalysts

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SUMMARY: Polyethylene with long-chain branches can be produced with certain metallocene catalysts, such as monocyclopentadienyl derivatives, by incorporation of macromonomers formed *in-situ* into the polymer backbone. This investigation demonstrates how dual metallocene systems can be used to control and enhance the level of long chain branching of polyethylene made with these catalysts. For instance, a catalyst that favors long chain branch formation, such as Dow's constrained geometry catalyst, can be combined with another metallocene that produces macromonomers at a faster rate. In this way, the concentration of macromonomers in the reactor increases, thus favoring the formation of long chain branches. This leads, however, to a complex microstructural control problem, since both the molecular weight and long chain branch distribution are affected simultaneously by the presence of the second catalyst. Several mathematical models will be used to describe this challenging microstructural control problem.

Introduction

Metallocene catalysts are unquestionably the most important development in the area of olefin polymerization since the discovery of Ziegler-Natta catalysts in the early fifties, since these catalysts permit the synthesis of polyolefins with uniform molecular properties. For instance, metallocenes produce polyolefins with the theoretical polydispersity index (PDI) of two for molecular weight distribution (MWD), as opposed to the large PDIs observed when heterogeneous Ziegler-Natta catalysts are used. Similarly, for the case of copolymerization of ethylene, propylene and higher α-olefins, copolymers with narrow and unimodal chemical composition distribution (CCD) are obtained, in contrast with the bimodal and non-uniform

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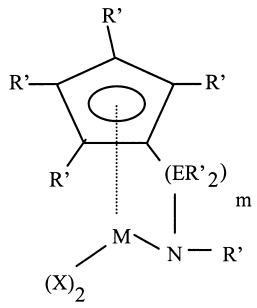
CCDs of copolymers made with heterogeneous Ziegler-Natta catalysts. There is general agreement that these differences are due to the fact that metallocenes are single-site catalysts, while heterogeneous Ziegler-Natta catalysts have two or more site types with different polymerization kinetic constants[1-4].

The single-site nature of metallocene catalysts permits the production of polyolefins with narrow MWD, which are generally considered to have excellent mechanical properties. Polyolefins with narrow MWD have greater dimensional stability, higher impact resistance, greater toughness at low temperatures, and higher resistance to environmental stress cracking. Unfortunately, polyolefins with narrow MWD are also very difficult to process. This has been considered to be one of the limiting factors to a wider application of metallocene-made polyolefins. Polyolefins with broader MWD and better processability can be produced with either two or more metallocenes in the same reactor or reactors in series but this, of course, leads to polymers with inferior mechanical properties.

Another remarkable feature of these catalysts is that some metallocene complexes can be used to synthesize polyolefins with long-chain branches (LCB). Lai et al.[5,6] used monocyclopentadienyl metallocene catalysts (**1**) (constrained geometry catalyst – CGC) to incorporate macromonomers, formed *in-situ*, into the polymer backbone. Macromonomers are dead polymer chains with terminal double bonds formed via β-hydride elimination. The presence of LCBs increases shear thinning and processability, while keeping the MWD narrow, with polydispersities typically between 2.0 to 2.5.



M – Ti, Zr, Hf
R' – hydrogen, silyl, alkyl, aryl
E – silicon or carbon
X – hydride, halo, alkyl, aryl
m – 1,2

1

Polyolefins made with this family of catalysts combine the excellent mechanical properties of narrow-MWD polymers with the good processability of broad-MWD polymers.

The mechanism of LCB formation with these catalysts is essentially terminal branching. Macromonomers formed *in-situ* are incorporated into the growing polymer chain according to the mechanism illustrated in Figure 1.

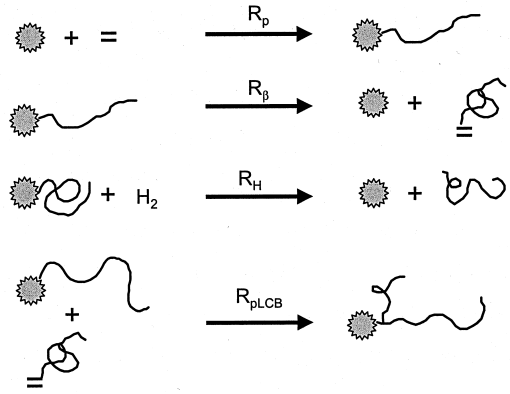


Fig. 1: Mechanism of LCB formation with metallocene catalysts. Dead polymer chains containing terminal vinyl unsaturation (macromonomers) can copolymerize with ethylene, forming LCBs.

Long Chain Branch Distribution for Single Metallocenes

It is evident from the polymerization mechanism shown in Figure 1 that the polymers made with these catalysts have a complex branching structure composed of comb and tree structures of different lengths. Soares and Hamielec[7,8] derived the following analytical solution for the multivariate distribution of molecular weight, chemical composition (for the case of copolymerization with α-olefins) and long chain branching for polymers made with these catalysts:

$$w(r,y,n)\mathrm{d}r\mathrm{d}y = \frac{1}{(2n+1)!} r^{2n+1}\tau^{2n+2}\exp(-r\,\tau)\mathrm{d}r \frac{1}{\sqrt{2\pi\,\beta/r}}\exp\left(-\frac{y^2 r}{2\beta}\right)\mathrm{d}y \qquad (1)$$

where, r is chain length, y is the deviation from the average mole fraction of monomer type 1 in the copolymer, $\overline{F}_1$, and n is the number of LCBs per chain. The parameter τ is defined as the ratio of all chain transfer rates to the propagation rate and the parameter β is related to the copolymerization reactivity ratios, r_1 and r_2, by the equation:

$$\beta = \overline{F}_1\left(1-\overline{F}_1\right)\left[1+4\overline{F}_1\left(1-\overline{F}_1\right)\left(r_1 r_2 - 1\right)\right]^{0.5} \tag{2}$$

Equation (1) is an extension of Stockmayer's bivariate distribution[9], which is valid only for linear chains, i.e. when $n = 0$. This equation permits one to obtain detailed information on the branching structure of these polymers that is not accessible experimentally. For instance, the MWD as a function of LCBs/chain is illustrated in Figure 2 for a given model homopolymer[7].

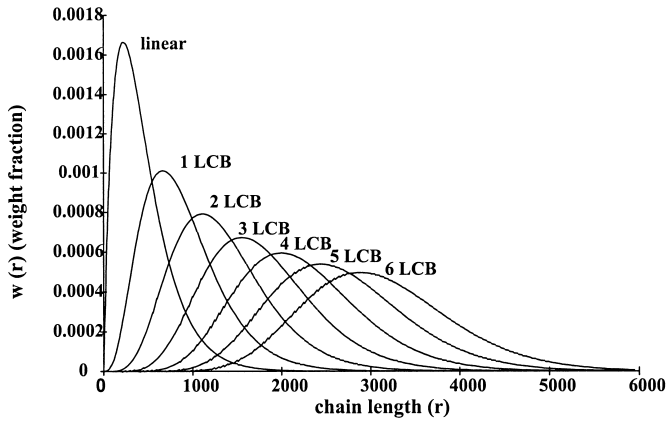


Fig. 2: MWD as a function of LCBs/chain predicted with Equation (1), normalized within each polymer population[7].

As expected, as the number of LCB per chain increases, so does the average molecular weight of a given polymer population, while PDI becomes increasingly smaller, as illustrated in Figure 3. This is just a consequence of the fact that macromonomers formed *in-situ* are reincorporated into the polymer chains via copolymerization with ethylene.

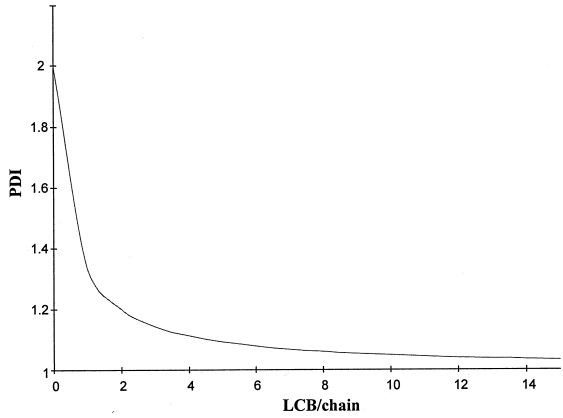


Fig. 3: Polydispersity index as a function of LCB per polymer chain[7].

Figure 2 shows the MWDs normalized for each LCB population. In fact, as indicated in Table 1, the fraction of chains containing several LCB/chain decreases very rapidly. This is also illustrated in Figure 4, where the MWD for the whole polymer is superimposed onto the MWD of each polymer population weighed by their respective weight fractions. As indicated, most polymer chains are linear. The chemical composition distribution of copolymers of ethylene, propylene and higher α-olefins can also be predicted with Equation (1), but is generally of less significance[8].

Table 1. Number and Weight Fractions of Linear and Branched Polymer Chains.

	number fraction	weight fraction
linear	0.8843	0.6792
1 LCB	0.0905	0.2095
2 LCB	0.0185	0.0715
3 LCB	0.0048	0.0256
4 LCB	0.0014	0.0094
5 LCB	0.0004	0.0035
6 LCB	0.0001	0.0013

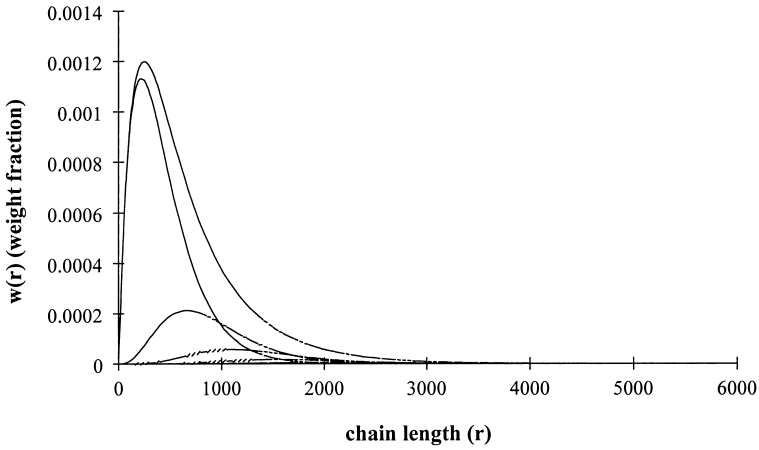


Fig. 4: Chain length distribution (CLD) as a function of LCBs/chain predicted with Equation (1), normalized for the MWD of the whole polymer[7]. The broadest curve is the CLD for the whole polymer. Underneath this curve, with decreasing areas, are the CLDs for linear chains, chains with one LCB per chain, two LCBs per chain, three LCBs per chain, etc.

It is also very important to be able to predict the branching structure of these polymer chains. Re-incorporation of linear macromonomer will lead to chains that contain comb branches. However, these branched chains can in their turn be terminated by β-hydride elimination forming branched macromonomers that upon polymerization will lead to polymer with branches on branches (tree structures), as indicated in Figure 5.

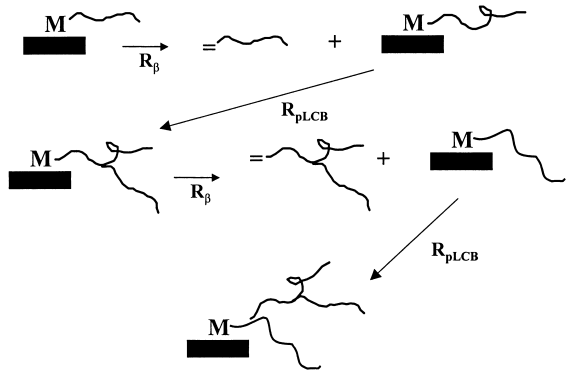


Fig. 5: Mechanism of formation of comb and tree branch structures.

Monte-Carlo simulation is ideally suited for determining the branch structure of these polymers. Beigzadeh et al.[10] developed a Monte-Carlo model to describe polymerization with this mechanism of branch formation and found out that most of the high molecular weight chains had branches on branches. Figure 6 indicates that, for this particular simulation, most chains with length greater than 20000 have branches and that most chains with length greater than 35000 have branches on branches (hyper-branched chains). This is a very important observation, since these hyper-branched structures are supposed to considerably enhance polymer processability[11,12]. Therefore, one might speculate that the excellent properties of polyolefins made with monocyclopentadienyl derivatives might be, at least in part, due to the presence of these hyper-branched polymer chains.

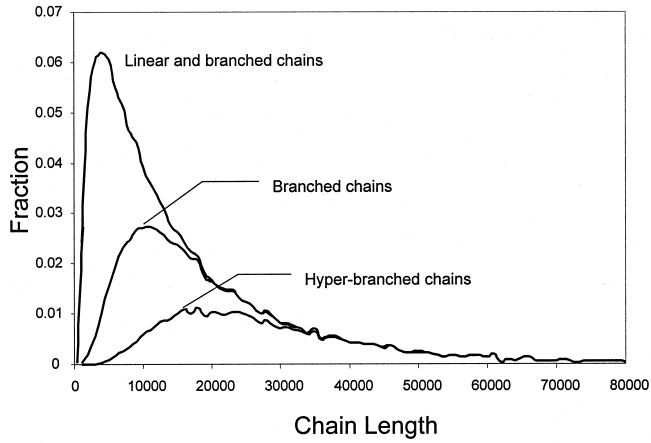


Fig. 6: LCB Structure as a function of molecular weight[10].

Long Chain Branch Distribution for Combined Metallocenes

The LCB frequency of polymers made with these catalysts can be enhanced by increasing the concentration of macromonomer present in the reactor, as clearly illustrated by the mechanism shown in Figure 1. For solution polymerization, there are essentially two ways of achieving this objective: (1) feed pre-formed macromonomer to the reactor, and (2) add a second catalyst with a higher rate of macromonomer formation to the reactor. Gas-phase polymerization has also been used to increase the concentration of macromonomers around the active site[13], but in this case chain mobility is evidently severely decreased.

Both alternatives are, in principle, capable of achieving the same LCB enhancement, provided that one assures that macromonomer concentration and reactor residence time distribution are the same. However, the use of two catalysts in the same reactor is very attractive due to its inherent simplicity. We will pursue this approach herein.

This concept is illustrated in Figure 7. A second metallocene (assumed to produce a negligible amount of chains with LCBs) is added to the reactor containing an LCB-forming catalyst such as CGC.

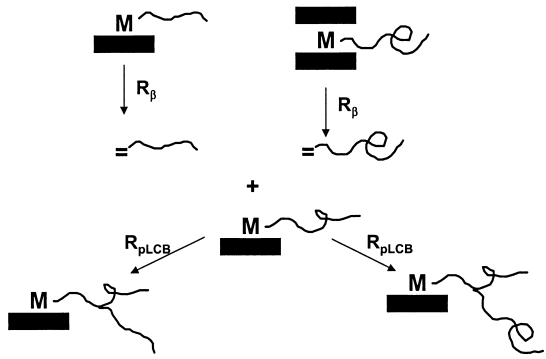


Fig. 7 : Enhancing LCB formation with combined metallocene catalysts.

It is crucial that the second catalyst be properly selected, so that LCB can be maximized. A simple expression for the overall LCB frequency of polymer made on a semi-batch reactor using two different metallocenes was derived by Beigzadeh[14]:

$$\overline{\lambda}_n = 500 \times \frac{\left[\left(k_{\beta 1} + k_{fm1} M\right) - \left(k_{\beta 2} + k_{fm2} M\right)\right] \; r + k_{\beta 2} + k_{fm2} M}{M\left[\left(k_{p1} - k_{p2}\right) r + k_{p2}\right] t} \times \left[t - \frac{1 - \exp\left(-k_{LCB}\, C\, r\, t\right)}{k_{LCB}\, C\, r} \right] \tag{3}$$

where $\overline{\lambda}_n$ is LCB per 1000 carbon atoms, C is the total catalyst concentration, r is the fraction of CGC present in the reactor, M is monomer concentration at the active site, t is

polymerization time, and k_β, k_{fm}, k_p, k_{LCB} are the rate constants for β-hydride elimination, transfer to monomer, propagation, and LCB incorporation, respectively.

This equation was used to generate the plot shown in Figure 8. It is very important to notice that the LCB frequency for the overall polymer passes through a maximum for a given fraction of CGC in the catalyst mixture only if the rate of macromonomer formation of the second catalyst is higher than that of CGC alone.

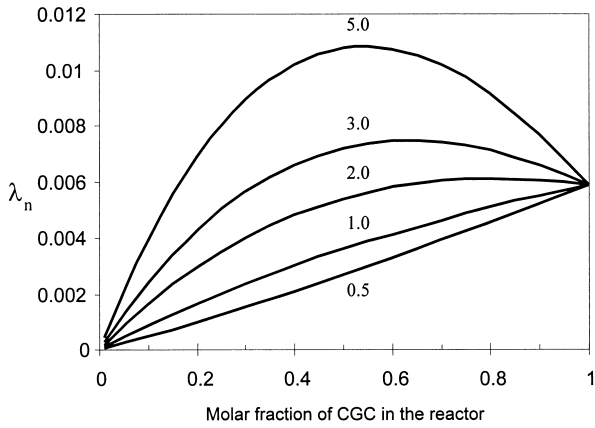


Fig. 8: Number of LCB/1000 carbon atoms as a function of CGC fraction in a binary catalyst mixture. Legends indicate the relative frequency of macromonomer formation of the second catalyst as compared to CGC[14].

Therefore, it seems that if CGC is combined with another adequate metallocene, LCB can be significantly increased. Evidently, since most of the polymer chains made by the second catalyst will remain unreacted, the MWD of the resulting polymer (and the CCD for the case of copolymerization) might also be significantly altered. Beigzadeh et al.[15,16] have developed dynamic and a steady-state models using population balances and the method of moments to investigate the effect of different metallocene combinations on the resulting MWD, CCD and LCB, but this work will not be discussed in details herein. It suffices to say that their findings agree with the results presented in Figure 8 and the experimental results presented in the next section.

Putting the Theory to Test – Enhancing LCB by Combining Two Metallocene Catalysts

Polymerization of ethylene was carried out in a 600 cm^3 autoclave reactor with a constrained geometry catalyst (CGC-Ti) and $Et[Ind]_2ZrCl_2$[17]. Measured amounts of tris(pentaflourophenyl)borane (TPFB) ([TPFB]/[Catalyst] = 100), MAO ([Al]/[Catalyst] = 500), and hydrogen (0-20 ml) 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+$Et[Ind]_2ZrCl_2$) was varied from 0 to 1.0. All of the polymerization runs were conducted at 140°C and 1792 kPa (260 psi) for 10 minutes and terminated by injecting acidic ethanol. The precipitated polymer was adequately washed with ethanol and dried in vacuum at 60°C for 10 hours.

Gel permeation chromatography (GPC) was used to determine the MWD of the samples. GPC runs were performed on a high temperature Waters 150CV Plus™ instrument with 1,2,4-trichlorobenzene (TCB) as solvent at 140°C. A universal calibration method 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 35wt% of polymer in solution). The polymer was dissolved at 150°C for 30 minutes 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 LCB frequency calculations were done according to the methodology proposed by Randall[18,19].

^{13}C NMR analysis of polyethylene samples synthesized with CGC-Ti and $Et[Ind]_2ZrCl_2$ individually showed that the concentration of terminal double bonds in polymer sample made with $Et[Ind]_2ZrCl_2$ was more than twice as much as that found for the sample made with CGC-Ti (Table 2). Therefore, $Et[Ind]_2ZrCl_2$ was used as the CGC-Ti partner in the combined

catalyst. Figure 9 shows a typical ^{13}C NMR spectrum for these samples, including peak assignments and the nomenclature used in Table 2.

Table 2. 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[17].

No.	**CGC-Ti** Mol%	NMR Data (area under the peak) $\alpha\delta^+$ carbon	Average of 1S, 2S,and 3S	Allylic Carbon (a)	Unsaturated / saturated chain ends	Total Carbon intensity	LCB per 10000 C[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

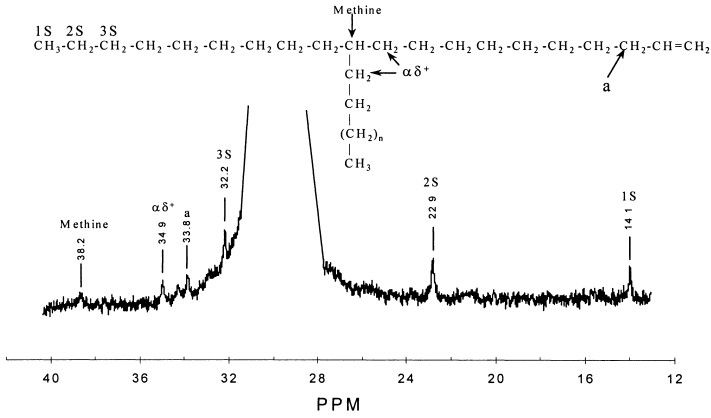


Fig. 9 : ^{13}C NMR spectrum of a typical polyethylene sample, including peak assignments.

Figure 10 illustrates how the number of LCB per 10000 carbon atoms depends on the fraction of CGC-Ti in the binary mixture. Three different hydrogen levels have been studied (notice

full 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, as predicted in Figure 8. No branching was observed when only $Et[Ind]_2ZrCl_2$ was used. As more CGC-Ti was employed in the binary catalyst system the measured LCB frequencies increased up to a maximum corresponding to a fraction of CGC-Ti equal to 50%. By increasing the mole fraction of CGC-Ti to more than 50%, the branching content started decreasing to the LCB content obtained when only CGC-Ti was used. As proposed by Beigzadeh et al.[16], this behavior can be attributed to a lower macromonomer concentration as the mole fraction of $Et[Ind]_2ZrCl_2$ decreases. Figure 10 also indicates that the observed optimum value for CGC-Ti mole fraction is independent of the amount hydrogen, as expected, since the β-hydride elimination reaction (which forms macromonomers that will produce LCB) is not affected by hydrogen concentration. This is also in agreement with the simulation results obtained by Beigzadeh et al.[16]

Figure 11 shows the MWD of polyethylene samples synthesized with the CGC-Ti/$Et[Ind]_2ZrCl_2$ combination. 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 $Et[Ind]_2ZrCl_2$.

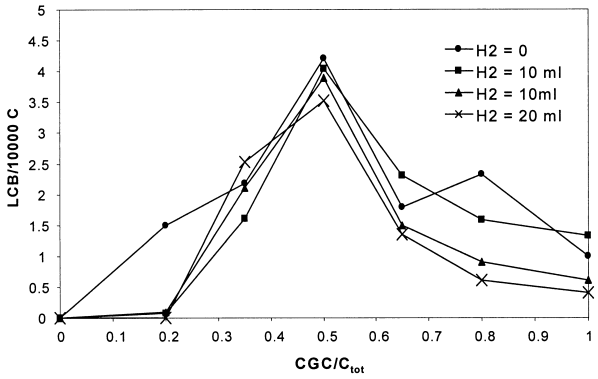


Fig. 10 : LCB enhancement by combining two metallocene catalysts[17].

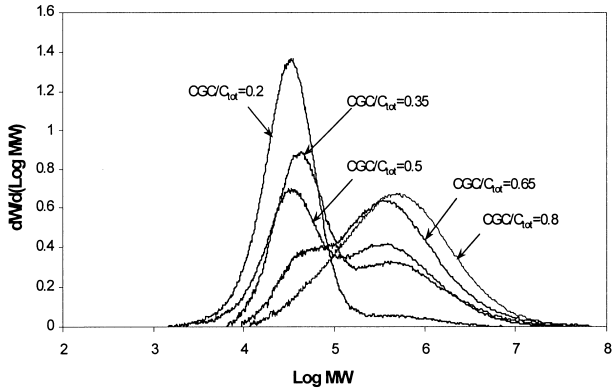


Fig. 11 : Molecular weight distributions for H_2 = 0 ml[17].

Even though Figures 10 and 11 indicate that the procedure adopted herein for LCB enhancement is feasible, it is clear from Figure 11 that to achieve the maximum possible LCB level for this particular catalyst combination at the studied conditions (CGC-Ti/C_{tot} = 0.5), one will produce polymer with broad and bimodal MWD. This is, in turn, contradictory to our original objectives of producing polymer with narrow MWD to ensure good mechanical properties.

However, this particular catalyst combination allows for quite flexible control of MWD breadth, since Et[Ind]$_2$ZrCl_2 has been shown to be less sensitive to H_2 pressure than CGC-Ti[20-23]. Therefore, upon increasing H_2 concentration, the molecular weight of polymer chains made on the CGC-Ti site decreases steadily, while the molecular weight of polymer made with Et[Ind]$_2$ZrCl_2 is not significantly affected. As a consequence the MWDs of polymers made with the two catalysts tend to superimpose, with consequent decrease in polydispersity index, as illustrated in Figures 12 and 13.

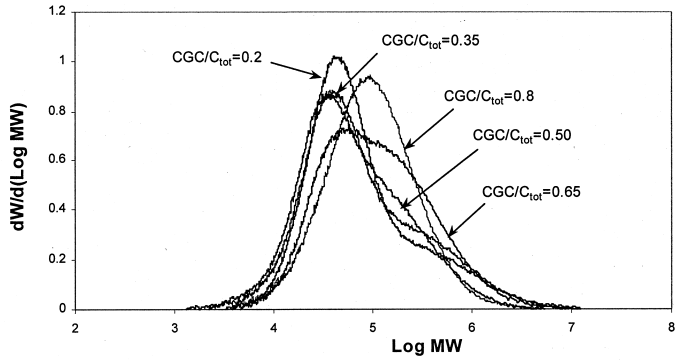


Fig. 12 : Molecular weight distributions for H_2 = 10 ml[17].

Therefore, since LCB frequency is not affected significantly by H_2 pressure, as indicated in Figure 10, this combined catalyst system can be used to control LCB and MWD independently, which is a truly unique feature of this particular catalyst combination.

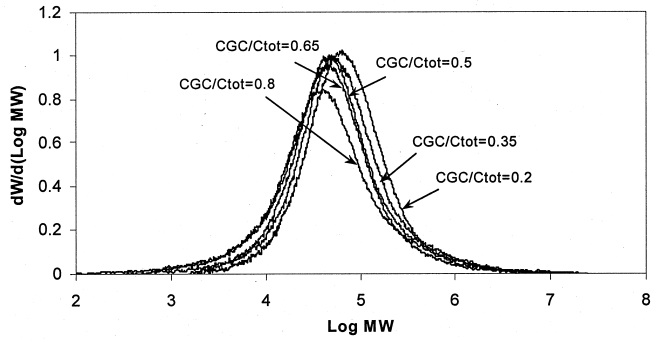


Fig. 13 : Molecular weight distributions for H_2 = 20 ml[17].

Enhancing LCB by Combining Two Metallocene Catalysts – Influence on Final Branching Structure

A final consideration should be made regarding the enhanced LCB degrees obtained when two metallocene catalysts are used simultaneously for polymerization and LCB formation. For this technique to be successful, most LCBs have to be produced by the catalyst that does not form branched polymer, as clearly indicated in Figure 8. As a consequence, the proportion of chains with comb structures will be higher than that present when a single CGC catalyst (or another LCB-forming catalyst) is used (Figure 14). It is well known that tree and comb branched polymer chains can have quite different rheological behaviours[11,12]. Therefore, the LCB enhancement obtained by combining two metallocene catalysts might affect the final rheological and mechanical properties of the polymer in a rather complex way. This investigation is currently under way in our research group and will be reported elsewhere.

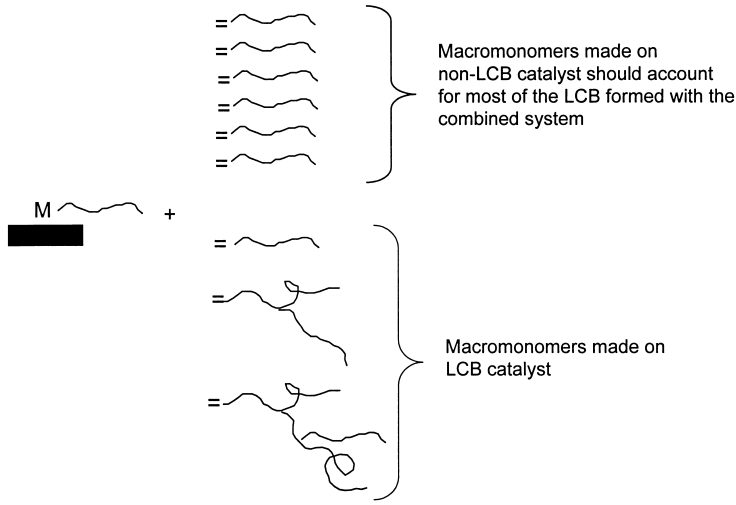


Fig. 14 : The described metallocene combination for LCB enhancement will favor the formation of comb-branched chains.

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