Macromol. Symp. **2004**, *213,* 69-78

Relative Reactivity Enhancement of $(Me_5Cp)_2ZrCl_2$ in Mixture with $(1,2,4\text{-}Me_3Cp)_2ZrCl_2$ during Ethene /1-Hexene Copolymerization

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Summary: Dual-site ethene/1-hexene copolymerizations with MAO-activated $(1,2,4\text{-}Me_3Cp)_2ZrCl_2$ and $(Me_5Cp)_2ZrCl_2$ catalysts were performed. Copolymers with narrow molecular weight distributions and bimodal short chain branching distributions could be produced. The combined catalyst system demonstrates a number of discrepancies from an expected average behavior of the individual sites. Dual-site $(1,2,4\text{-}Me_3Cp)_2ZrCl_2/(Me_5Cp)_2ZrCl_2$ systems produce copolymers with lower incorporation than expected. Clear evidences for relative activity enhancement of the $(Me_5Cp)_2ZrCl_2$ catalyst in the mixture were observed in melting endotherms and Crystaf profiles. Molecular weights obtained by the mixture were higher than for any of the individual catalysts. A similar effect is observed for a dual-site system of the $(1,2,4\text{-}Me_3Cp)_2ZrCl_2$ catalyst together with the $Me_4Si_2(Me_4Cp)_2ZrCl_2$ catalyst as an alternative to $(Me_5Cp)_2ZrCl_2$.

Keywords: bimodal; catalyst mixture; copolymerization; dual-site; metallocene catalysts

Introduction

Metallocenes are known as single-site catalysts. They produce polymers with narrow molecular weight distributions (MWD), and copolymers with narrow distributions of short chain branches (SCBD). Combination of two metallocenes with known polymerization behavior can be used to control polymer microstructure. Polyethene homopolymers with broader and sometimes bimodal MWD can be obtained.[1-4] Concerning copolymerization with a mixture of two metallocenes there are, to our knowledge, only a few reports in the literature.[5-7] Common to these studies was no observation of interaction between the two different sites, e.g. by re-adsorption of a terminated chain at the alternative site. Such reports have been issued, however, for polymerization of propene. Combinations of metallocenes

DOI: 10.1002/masy.200450908

with different stereospecifities have produced stereoblock polymers.[8-11] The stereoblock polymer is a cross product resulting from interaction of the two different sites during chain growth. Lieber and Brintzinger[11] have proposed that the transfer of a growing polymer chain occurs through an exchange of polymer chain between Zr centers and the Al center of the cocatalyst.

In the present investigation, we carried out ethene/1-hexene copolymerization catalyzed by the following methylaluminoxane (MAO)-activated zirconocene catalysts: $(1,2,4\text{-}Me_3Cp)_2ZrCl_2$ (abbreviated as $1,2,4\text{-}Me_3Cp$), $(Me_5Cp)_2ZrCl_2$ (abbreviated as Cp*) and mixtures of these two catalysts. The influence of the dual-site catalyst on polymerization activity, incorporation of comonomer and polymer microstructure has been studied and compared with the individual catalysts at corresponding polymerization conditions.

Experimental

Chemicals. Bis(1,2,4-trimethylcyclopentadienyl)zirconium dichloride and bis(pentamethyl-cyclo-pentadienyl) zirconium dichloride purchased from Boulder Scientific Co., 10 wt% MAO in toluene purchased from Albemarle S.A., nitrogen (99.999%) purchased from Hydrogas, and ethene (polymerization grade) and 1-hexene (polymerization grade) donated from Borealis were all used as received. Toluene (p.a.) purchased from Merck was refluxed over sodium/ benzophenone and distilled under nitrogen atmosphere before use.

Polymerization. The polymerizations were performed in a steel autoclave that was repeatedly flushed and evacuated both with nitrogen and ethene. The reactor temperature was set (80 °C), and toluene (200 mL) was introduced. For copolymerizations, the desired amount of 1-hexene was added immediately after the toluene. The stirring rate was set (2000 rpm), and the reactor was pressured with ethene to the wanted total pressure (2 bar). Ethene was then equilibrated before the MAO solution was added. After 7 min the catalyst dissolved in toluene was injected. The total amount of catalyst was 0.23 μmol, and the Al/Zr ratio was 3000. The total pressure was held constant during the reaction, and the instantaneous consumption of ethene was measured. Polymerization time was 1 hour. The polymer product was poured into a mixture of methanol (300 mL) and hydrochloric acid (30 mL) and stirred overnight. After filtration the polymer was washed with methanol and dried in air.

Characterization. Differential scanning calorimetry (DSC) with a Perkin-Elmer 7 series thermal analyzer, gel permeation chromatography (GPC) with a Polymer Laboratories PL-210 GPC instrument and Fourier transform infrared spectroscopy (FTIR) with a Bruker IFS66V spectrophotometer were performed according to previously reported procedures.[12] Crystallization analysis fractionation (Crystaf) was performed with a model 200 Crystaf instrument manufactured by Polymer Char. The instrument is equipped with five separate stainless steel crystallization vessels for the simultaneous analyses of five different samples. The polymer samples (10.2 ± 0.8 mg) were dissolved in TCB (48 ml) at 160 °C for 60 min, and then the solution was equilibrated at 95 °C for 45 min. Subsequently, the solution was cooled at a rate of 0.10 °C/min to 30 °C. The solution was sampled 50 times at temperature intervals between 95 °C and 30 °C, and the change in polymer concentration in solution with temperature was monitored by a in-line infrared detector.

Results and Discussion

The Cp* catalyst has high starting copolymerization activity, but the activity decay is very fast. The average copolymerization activity of this catalyst is therefore low, and it is approximately six times lower than for the 1,2,4-Me_3Cp catalyst. The 1:1 mixture of these two catalysts has an activity in between the activities of the individual catalysts, as shown in Figure 1a. Because of the large difference in activities for the individual catalysts it might be expected that the mixture results in polymer properties close to the properties obtained by 1,2,4-Me_3Cp.

The incorporation was determined by FTIR. Figure 1b shows that 1,2,4-Me_3Cp incorporates significantly more 1-hexene than Cp*. The 1:1 mixture results in properties intermediate between the two individual catalysts, but the 1-hexene content certainly is lower than expected from the six-fold higher activity of the 1,2,4-Me_3Cp catalyst.

If the two catalysts in the dual-site system behave independently, the incorporation for the mixture can in principle be predicted from the incorporations for the individual catalysts taking into account their different activities. Other mixtures than 1:1 have been utilized in copolymerizations with similar initial 1-hexene concentration. Figure 2 shows the incorporation as a function of the mole fraction of Cp* in mixture with 1,2,4-Me_3Cp. By comparing the obtained and the predicted incorporations, it can be seen that each of the

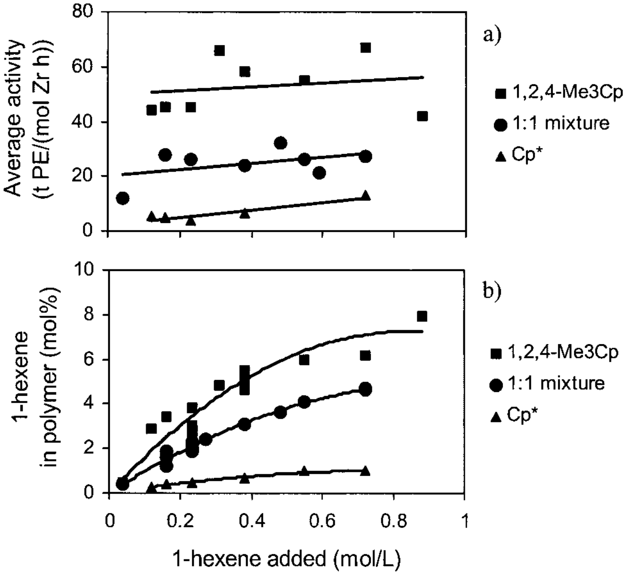

Figure 1. Average activities obtained for 1,2,4-Me_3Cp, Cp* and the 1:1 mixture of these two (a) and incorporation of 1-hexene in poly(ethene-*co*-1-hexene) (b) as a function of initial 1-hexene concentration. Cocatalyst = MAO; T = 80 °C; P_{total} = 2 bar; $n_{Zr\ tot}$ = 0.23 μmol; Al/Zr_{tot} = 3000.

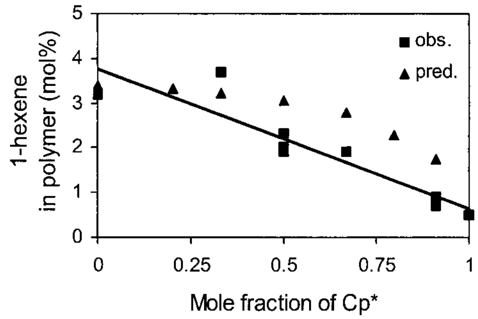

Figure 2. Observed (obs.) and predicted (pred.) incorporation of 1-hexene as a function of the mole fraction of Cp* in mixture with 1,2,4-Me_3Cp. Cocatalyst = MAO; T = 80 °C; P_{total} = 2 bar; $[1\text{-hexene}]_{initial}$ = 0.23 mol/L; $n_{Zr\ tot}$ = 0.23 μmol, Al/Zr = 3000.

mixtures (with one exception) results in poly(ethene-*co*-1-hexene) having lower comonomer content than expected. When less 1,2,4-Me_3Cp (and then more Cp*) is present in the mixture, the 1-hexene content decreases. However, the decrease is larger than expected taking into consideration the much higher activity of the 1,2,4-Me_3Cp catalyst.

The 1:1 mixture produces copolymers with two distinct melting endotherms when 0.23 – 0.72 mol/L 1-hexene was added, as illustrated in Figure 3. This is in accordance with a copolymer with two different fractions of comonomer. The high temperature peak is attributed to the Cp*-site, and the low temperature peak to the 1,2,4-Me_3Cp-site. When low amount of 1-hexene was added (0.16 mol/L), the copolymer has only one melting peak, possibly because the melting of the two fractions now occurs so close in temperature that they do not separate into two peaks. The low temperature peak moves towards lower temperature as the 1-hexene content increases, while the high temperature peak is approximately constant, or increases slightly when higher initial 1-hexene concentration was used. This may be caused by some cocrystallization of the two polymer fractions for low 1-hexene content. High comonomer concentration leads to polymer fractions with larger differences in their comonomer content, and thereby easier separation in the crystallization process.

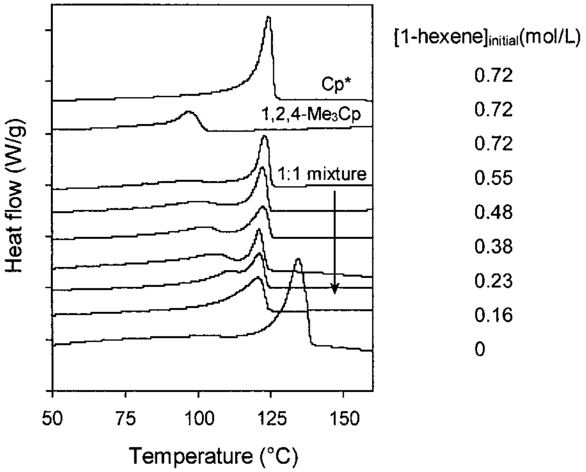

Figure 3. Melting endotherms for polyethene and poly(ethene-*co*-1-hexene) made with the 1:1 mixture and melting endotherms for poly(ethene-*co*-1-hexene) made with the individual catalysts for comparison.
Cocatalyst = MAO; T = 80 °C; P_{total} = 2 bar; $n_{Zr\,tot}$ = 0.23 μmol; Al/Zr_{tot} = 3000.

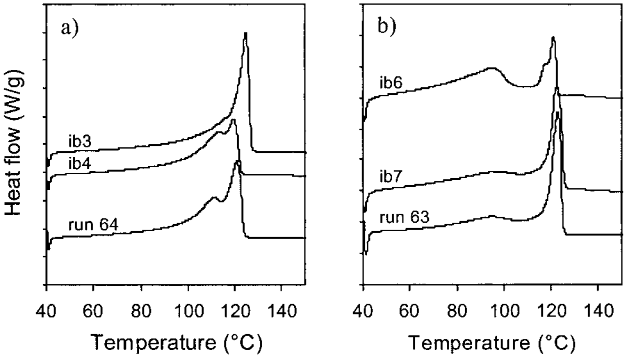

Figure 4. Comparison of melting endotherms for copolymers made with the 1:1 mixture (runs 63 and 64) and endotherms of blended copolymers made with 1,2,4-Me_3Cp and Cp* individually. Cocatalyst = MAO; T = 80 °C; P_{total} = 2 bar; $n_{Zr\ tot}$ = 0.23 μmol; Al/Zr_{tot} = 3000.
(a) $[\text{1-hexene}]_{initial}$ = 0.23 mol/L; ib3 = 50/50 wt% blend; ib4 = activity ratio blend.
(b) $[\text{1-hexene}]_{initial}$ = 0.72 mol/L; ib6 = activity ratio blend; ib7 = 50/50 wt% blend.

A closer look at the melting endotherms shows that the influence of the Cp*-based polymer fraction is much stronger than expected from the individual activities clearly pointing to an in-situ enhancement of the activity of the Cp*-site. To check this effect further, polymers made with the individual catalysts were blended by dissolution in hot xylene and then coprecipitated in cold methanol. The polymers were blended in accordance with the individual activity ratio and in a 50/50 wt% mixture. The melting curves of these blends are compared with the melting curves for copolymers made by the 1:1 mixture using similar 1-hexene concentrations. Figure 4 shows that the behavior of the polymer from the mixture is between what is expected from the activity ratio and a 50/50 wt% blend, and rather closer to the latter.

The weight-average molecular weights (Mw) for poly(ethene-*co*-1-hexene) made with 1,2,4-Me_3Cp, Cp* and the 1:1 mixture were determined by GPC. Figure 5 shows that Cp* and 1,2,4-Me_3Cp produce copolymers with quite similar Mw, but 1,2,4-Me_3Cp gives copolymer with rather high Mw for the high comonomer content. The 1,2,4-Me_3Cp catalyst has in principle many conformations due to the possibility of relative rotation of the ligands. It turns out, however, that one specific conformer is the most stable one. This structure is rather open towards coordination of the monomers, but at the same time it contains one methyl on each

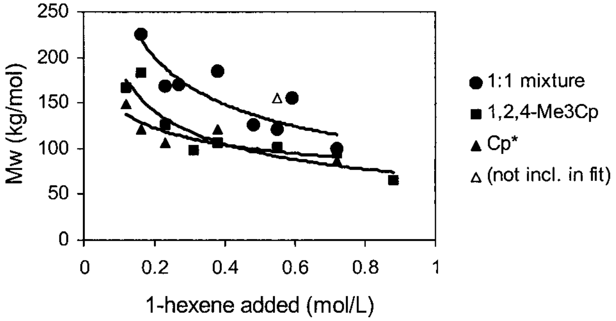

Figure 5. Mw for poly(ethene-*co*-1-hexene) as a function of initial 1-hexene concentration. Catalysts = 1,2,4-Me_3Cp, Cp*, and 1:1 mixture of these two; cocatalyst = MAO; T = 80 °C; P_{total} = 2 bar; $n_{Zr\,tot}$ = 0.23 μmol; Al/Zr_{tot} = 3000.

ligand that efficiently prevents rotation between the γ-agostic and β-agostic states after 1-hexene insertion.[13] Such a rotation is a necessary step in the termination sequence. As a result, 1,2,4-Me_3Cp incorporates 1-hexene unusually easy with a simultaneous low termination frequency.

It is remarkable that Mw for copolymers made with the 1:1 mixture consistently, with only one exception, is higher than for both the individual catalysts (Figure 5). This is highly unexpected since earlier experimental evidence indicates that each metallocene in a mixture behaves as if present alone in the reactor.[1-3] This observation indicates that the two catalysts in the mixture seem to influence each other's behavior. One possible explanation for the observed high molecular weights can be deduced from previous reports stating that chain transfer to trimethylaluminum (TMA) is important for Cp*.[14-15] The chains originating at Cp* contain minimal comonomer, but terminate frequently with TMA. Thus these chains can fairly easy be incorporated into the more open 1,2,4-Me_3Cp-site and continue to polymerize. This mechanism is in analogy to the model discussed by Lieber and Brintzinger[11] for propene polymerization by mixture of two metallocenes with different stereospecifities. The Mw for polymer prepared by the 1:1 mixture followed the normal decreasing trend with higher comonomer content, while the number-average molecular weight (Mn) from GPC was more constant.[12] Consequently, the MWD became more narrow as the 1-hexene content increased. It is noteworthy that by combining two metallocenes a very narrow MWD can be observed from polymer chains that differ dramtically in their comonomer content. Chain

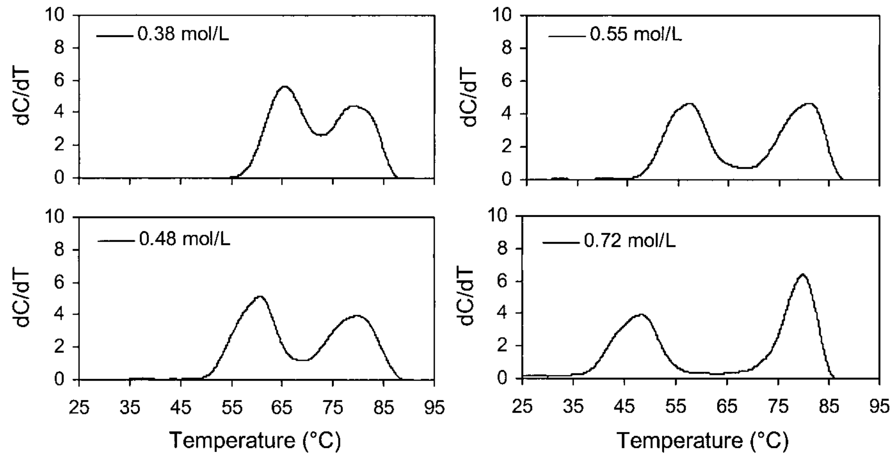

Figure 6. Crystaf profiles for poly(ethene-*co*-1-hexene) samples made with 1:1 mixture of 1,2,4-Me_3Cp and Cp* using different initial 1-hexene concentration. Cocatalyst = MAO; T = 80 °C; P_{total} = 2 bar; $n_{Zr\,tot}$ = 0.23 μmol; Al/Zr_{tot} = 3000.

transfer to TMA is an important termination mechanism for the homopolymer, but it gets less important as the 1-hexene content increases.[12] Chain transfer to TMA probably gets less important as these chains may continue to polymerize on the other site, alternatively TMA has to compete with 1-hexene for access to the active site.

In order to eliminate the possibility in the dual-site system of ligand exchange reactions, possibly resulting in a mixed ligand catalyst, we have as an alternative to Cp*, studied the $Me_4Si_2(Me_4Cp)_2ZrCl_2$ catalyst (abbreviated as aMe_4Cp). The geometry resembles that of Cp*, but the opening angle is 4° larger and the conformation approaches an eclipsed one.[16] The polymerization behavior is very much the same for both catalysts, although the bridged one gives increased termination probability after 1-hexene insertion, but less frequent termination after ethene insertion. The 1:1 mixture of 1,2,4-Me_3Cp and aMe_4Cp also produced poly(ethene-*co*-1-hexene) with higher Mw than for the individual catalysts at intermediate 1-hexene concentrations. In addition lower comonomer incorporation, than expected from the ca. 10:1 activity ratio between the individual catalysts, was observed. In the melting endotherms a significant overrepresentation of the high temperature melting peak, due to the

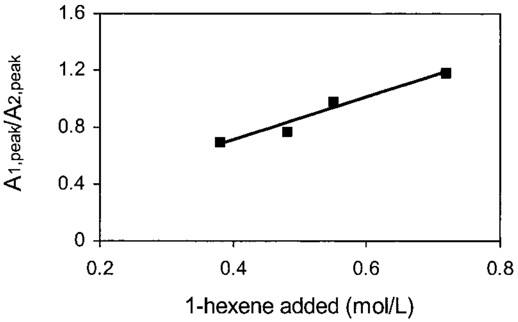

Figure 7. Ratio between weight fraction of polymer within high ($A_{1,peak}$) and low ($A_{2,peak}$) crystallization peaks for poly(ethene-*co*-1-hexene) made with the 1:1 mixture as a function of initial 1-hexene concentration.

aMe$_4$Cp catalyst, was observed.

Crystaf of poly(ethene-*co*-1-hexene) made with the 1:1 mixture of 1,2,4-Me$_3$Cp and Cp* was performed to determine the short chain branching distribution (SCBD). Examples of Crystaf profiles are given in Figure 6, and as illustrated bimodal SCBDs were obtained. The high temperature peak results from crystallization of polymer chains with few short chain branches, and these are attributed to the Cp*-site in the mixture. The low temperature peak results from crystallization of polymer chains made with the 1,2,4-Me$_3$Cp-site, and these chains contain many short chain branches. Once more, a significant contribution from the Cp*-site is observed.

The ratio between the fractions of polymer within the high and low crystallization peak temperatures ($A_{1,peak}/A_{2,peak}$) increases with increasing initial 1-hexene concentration, as illustrated in Figure 7. The relative activity of the Cp* catalyst in the mixture increases almost linearly with the 1-hexene concentration.

Conclusion

The dual-site 1,2,4-Me$_3$Cp/Cp* system demonstrates a number of discrepancies from an expected average behavior of the individual catalysts. The most striking result is Mw higher than for both the individual catalysts. Other observations were lower comonomer incorporation than expected, a much more pronounced melting/crystallization peak ascribed to Cp* than the activities predicts, and gradual elimination of chain transfer to TMA with increasing 1-hexene concentration. The data are interpreted as an enhanced activity of the Cp*-site relative to the 1,2,4-Me_3Cp-site possibly coupled with chain transfer from the Cp*-site to the 1,2,4-Me_3Cp-site. However, we do not believe that a full explanation of the unexpected relative activity enhancement of one of the sites can be given at this point. Further investigations clearly are needed.

Acknowledgement

Financial support from Borealis AS is gratefully acknowledged. We would also like to thank Professor Joao B. P. Soares at the University of Waterloo, Canada for allowing I. Bruaseth to visit his group to do Crystaf analyses.

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