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Ethylene/1-Butene Copolymerization over Heterogeneous Metallocene Catalyst

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Summary: Nowadays, bimodal polyethylene obtained in a two step cascade process is a matter of intensive research in polyolefin field. In the second stage of this process, a high molecular weight ethylene-α-olefin copolymer is formed over the homopolymer produced in the first step. In this work, a study of reaction variables on this second step using an heterogeneous metallocene catalyst was carried out. The effect of reaction temperature (70–85 °C) and comonomer concentration (0–0.32 mol/l) was evaluated. Polymerization results showed that activity increases with temperature and 1-butene initial concentration. Moreover, higher comonomer concentrations and lower temperatures involve higher short chain branching (SCB). Copolymers characterization indicated that melt temperature and density values have a lineal decrease with the SCB content in the polymer, regardless of the reaction temperature. As well, for every temperature, higher comonomer concentrations do not seem to affect to molecular weight, whereas a decrease of crystallinity was observed, which may explain the increase of catalyst activity.

Keywords: comonomer incorporation; copolymerisation; metallocene catalysts; polyethylene

Introduction

Advances on polymerization technology and catalyst development allow nowadays the production of bimodal polyethylene with improved properties, widening the market through new applications. It is constituted by two fractions with different molecular weight distribution and comonomer content obtained mainly in a two step cascade process. In the first stage ethylene is polymerized using hydrogen to control chain length. After hydrogen removal, a high molecular weight ethylene-α-olefin copolymer is formed over the homopolymer in a second step. The result is a reactor blend which combines, on the one hand, good properties of stiffness and processability from the homopolymer and toughness, impact strength and stress crack resistance from copolymer on the other hand.[1–6]

Cascade processes present heavy requirements for catalysts such as high activity in each step conditions, long polymerization lifetime, good hydrogen and comonomer response and good polymer morphology. Ziegler–Natta catalysts are conventionally used to obtain bimodal polyethylene[7] but it is known that metallocene catalysts present several advantages in olefin polymerization, especially in ethylene copolymerization with α-olefins.[6] Some of these advantages are more effective comonomer incorporation, narrower molecular and chemical composition distributions and higher homogeneity of branching distribution.[8,9]

Although ethylene/α-olefins copolymerization has been widely investigated using

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soluble metallocene catalysts, their industrial application in slurry and gas phase reactors requires an heterogeneization process consisting in supporting them on inert carriers like silica or alumina.[10] Several works have showed that metallocene immobilization over silica/methylaluminoxane (MAO) allow to keep the catalyst single–site character.[8,10,11] In this work, rac-Et$(IndH_4)_2$ zirconocene catalyst supported over silica/MAO was studied in ethylene/1-butene copolymerization, simulating the second stage of a cascade process for bimodal polyethylene production. Effects of reaction temperature and comonomer concentration on catalytic activity and products properties were evaluated.

Experimental Part

Ethylene and 1-butene (Air Liquide) were copolymerized at 8 bar in a 2 liter stainless-steel stirred reactor operating in slurry conditions and semi-batch mode using n-heptane (Scharlab) as solvent. The isothermal condition was controlled by means of an oil bath. Monomers and solvent were previously desoxygenated and dried by columns containing R-3/15 BASF catalyst, alumina and 3 Å molecular sieve. In a typical copolymerization, tri-isobutylaluminium (TIBA, Witco) was added to one liter of n-heptane acting as scavenger until a final concentration of 300 ppm is reached, and after that 1-butene was introduced into the reactor. Then, 30 mg of the catalyst (rac-ethylenebis(tetrahydroindenyl) zirconium dichloride supported over silica/MAO with a 0.2 wt % of Zr, Albemarle) was added to start the reaction. Ethylene was fed as it was demanded to keep a total pressure of 8 bar. After 1 hour, the reaction was stopped by depressurization and quenched by addition of acidified methanol. The product was filtered and dried at atmospheric pressure and 70 °C. Copolymerization activities were expressed as Kg PE/mol_{Zr} h.

Mean Molecular weights and distributions of the polymers were determined by size-exclusion chromatography at 145 °C on a Waters GPCV 2000 instrument, using 1,2,4-trichlorobencene as mobile phase. The column set consisted of two PL-Gel 10 μm MIXTED-B (300 mm × 7.5 mm) and one Polymer PL-Gel 10 μm 10E6 Å (300 mm × 7.5 mm). The columns were calibrated with 11 polystyrene standards (narrow molar mass distribution in the range: 3000–2 500 000) and with one high polydispersity polyethylene standard (from NIST, Mw = 53 070). 1-Butene content in copolymers was calculated with the Randall method[12] applied to ^{13}C-NMR (75 MHz) spectra obtained in a Bruker spectrometer at 90–100 °C using 1,2,4-trichlorobenzen as solvent. Differential scanning calorimetries were performed in a METTLER TOLEDO DSC822 equipment using a heating rate of 10 °C/min to determine the melting points and the crystallinities of copolymers. The density of copolymers was measured as described in ISO 1183. CRYSTAF analyses were carried out in a 200+ PolymerChAR apparatus to estimate the distribution of comonomer in the PE chains. Samples were dissolved at 160 °C in 1,2,4-trichlorobenzene at 0.5 mg/ml, stabilized at 95 °C and then cooled to 35 °C at 0.1 °C/min. Micrographs of copolymers were obtained with a Phillips XL30 ESEM (Environmental Scanning Electron Microscope) equipped with a tungsten filament and an accelerating voltage of 15 kV.

Results and Discussion

Table 1 shows the copolymerization results obtained with the heterogeneous metallocene catalyst at different temperatures and 1-butene initial loadings. The main properties of the resulting polymers (SCB content, density, molecular weight, polydispersity index, melting temperature and crystallinity) are also presented.

The activity increases with reaction temperature and initial amount of comonomer. Also higher 1-butene concentrations and lower temperatures involve higher SCB contents. These trends are clearly showed

Table 1.
Ethylene/1-butene copolymerization results obtained with the heterogeneous metallocene catalyst.

Test	$T_{reaction}$	$[C_4^=]$	Activity	SCB[a)]	Density	Mw	PDI	T_m	α[b)]
	(°C)	(mol/l)	(10^3 Kg/mol_{Zr}h)	(%)	(g/cm^3)	(g/mol)		(°C)	(%)
1	70	0.00	38	0.00	0.945	430000	6.03	135	62
2	70	0.05	74	1.29	0.923	390000	5.45	120	42
3	70	0.11	113	1.62	0.920	400000	5.08	117	41
4	70	0.16	167	2.37	0.912	410000	5.29	112	37
5	70	0.21	193	2.36	0.917	410000	4.48	113	37
6	70	0.27	185	2.41	0.918	440000	4.24	113	36
7	70	0.32	186	2.97	0.910	410000	4.30	109	32
8	80	0.00	81	0.00	0.923	410000	5.31	133	57
9	80	0.05	102	1.02	0.928	360000	4.84	122	46
10	80	0.11	164	1.30	0.925	380000	4.40	120	42
11	80	0.16	152	1.47	0.921	370000	4.44	119	42
12	80	0.21	138	1.95	0.920	390000	4.40	116	39
16	80	0.27	175	2.04	0.922	380127	4.28	115	39
14	85	0.00	86	0.00	0.944	310000	4.76	135	63
15	85	0.05	196	0.86	0.924	360000	3.79	124	47
16	85	0.11	241	1.15	0.922	290000	3.64	122	45
17	85	0.16	163	1.59	0.917	350000	3.52	118	42

[a)] Short Chain Branching content (mol %);
[b)] α, crystallinity determined from DSC results.

in Figure 1. The increase of activity with the reaction temperature is related to the increase kinetic and diffusion constants. The effect of comonomer concentration over the activity could be related with a better diffusion of the monomers through a less crystalline polymer shell formed around the active sites during the reaction.[13–15] This positive effect on the activity was clearly observed until certain value of 1-butene loading is reached (0.21 mol/l at 70 °C, 0.16 mol/l at 80 °C and 0.11 mol/l at 85 °C). For higher comonomer concentrations, the activity remains almost constant at 70 and 80 °C and even a decrease was detected working at 85 °C. This behaviour has been previously reported by several authors using supported metallocene catalysts[16,17] and it is usually attributed to a decrease in the propagation rate associated

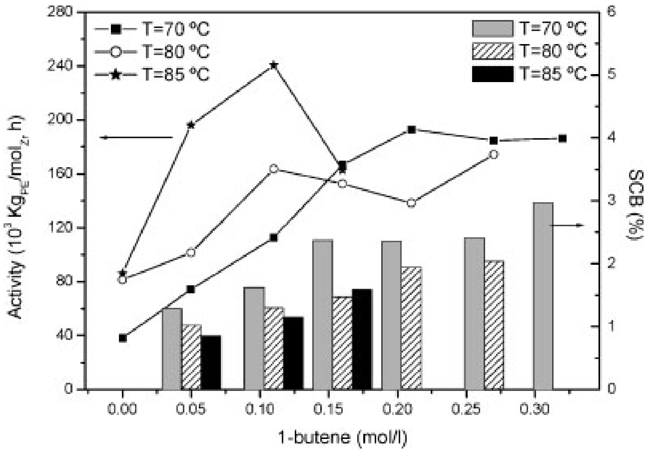

Figure 1.
Activity and percentages of SCB obtained at different temperatures and comonomer concentrations.

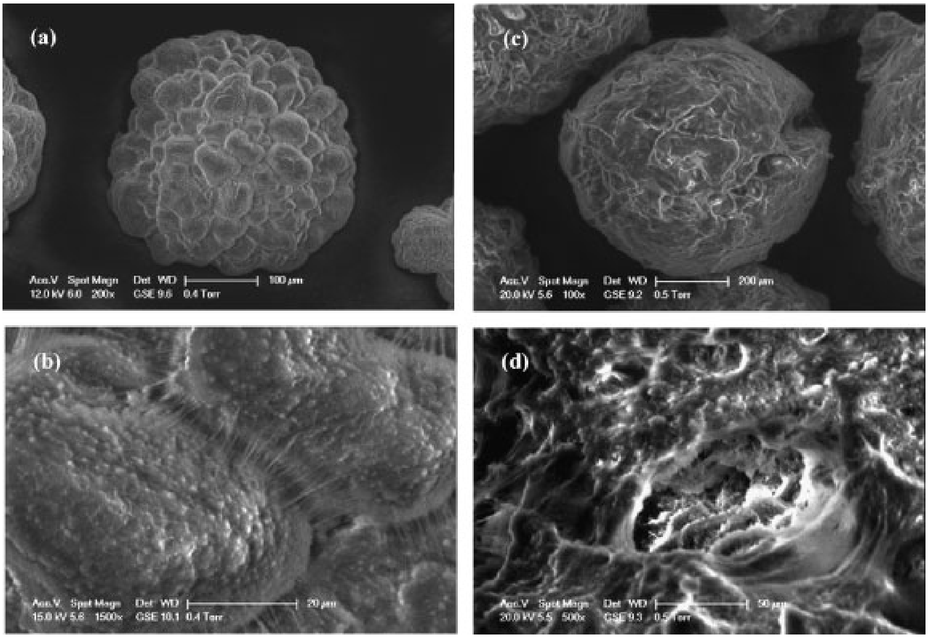

Figure 2.
SEM images of polymers corresponding to (a, b) test 14 and (c, d) test 17.

with the presence of higher comonomer content of the first shells of the polymer formed around the catalyst particles.

Morphological properties of homopolymers and copolymers were evaluated by means of scanning electron microscopy. Figure 2 displays SEM pictures of polymers produced in test 14 (homopolymer, images a and b) and 17 (copolymer with high content of 1-butene, images c and d). The images selected are representative of a general trend observed, where the use of 1-butene as comonomer yields a polymer with less evidence of stretched fibrils. Their presence have been associated with diffusion limitations,[18] supporting as possible reason the beneficial effect of comonomer on the activity related with the better monomers diffusion during the reaction, as it was suggested previously.[13–15] Besides, it is well known that mass transfer restrictions lead to broader molecular weight distributions.[19,20] In this sense, data of Table 1 show a decrease of polydispersity increasing 1-butene content of polymers that could be related with a lower mass transfer limitation.

The growth of comonomer incorporation observed when decreasing the reaction temperature could be related to the different influence on the insertion rate for both monomers. In this sense, Pietikäinen and coworkers observed a similar behaviour studying the effect of reaction temperature on the copolymerization of ethylene with several dienes.[21,22] These authors showed that the decrease in reaction temperature from 80 to 50 °C led to a higher amount of diene in the product since the reactivity of ethylene decrease more strongly than the reactivity of dienes. Similar trend seems to be observed in this case but using 1-butene as comonomer. On the other side, temperature changes involve different diffusivities for the comonomers which can alter the chemical composition around active centres, modifying the 1-butene incorporation.[10,23]

According to Table 1, a higher amount of 1-butene incorporated in the copolymer leads to a drop of density, melting temperature and crystallinity. Figure 3 and 4 show the dependence of polymers melting points and density with the SCB content, respec-

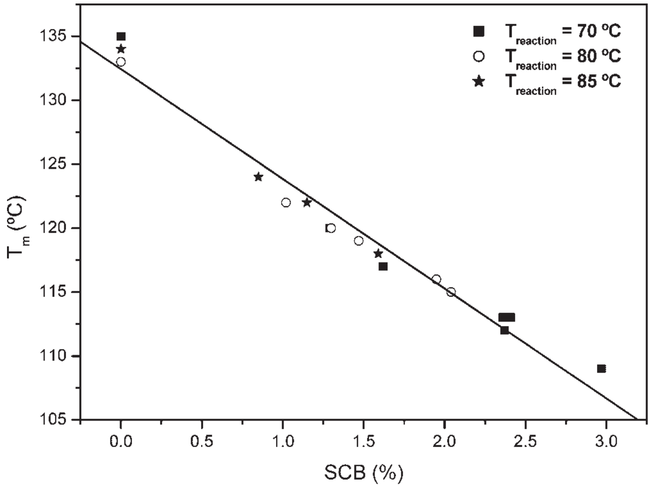

Figure 3.
Variation of polymers melting points with the SCB content.

tively. As can be seen, both properties displayed a linear decrease with increasing comonomer content in the polymer, regardless of the reaction temperature. At least, two main conclusions can be extracted from these graphs. First, almost the same polymer is obtained at different temperatures if the SCB content is similar, for instance, comparing tests number 2 and 10 (temperature reaction = 70 and 80 °C respectively, see Table 1). The only difference among both tests is that the reaction performed at higher temperature (10) needs a higher 1-butene concentration in the reactor to obtain the same SCB content in the polymer. As explained above, changes of monomers reactivity and diffusivity induced by the reaction temperature could cause this behaviour. The second conclusion is that a very small amount of 1-butene in the reactor leads to an important decrease of density, crystallinity and melting point of the polymer. These results show a significant advantage of metallocene catalysts with

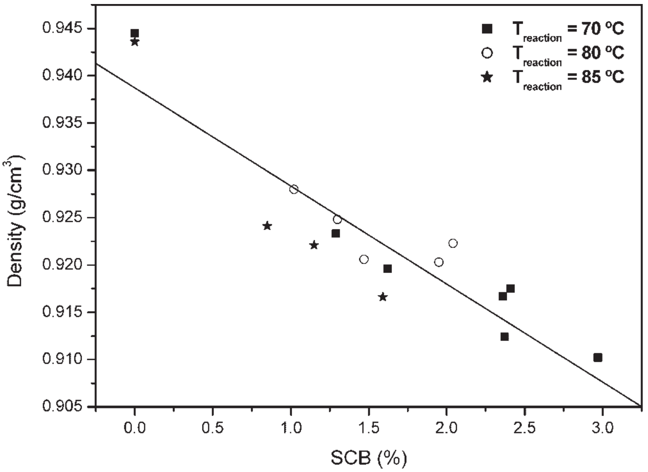

Figure 4.
Variation of polymers density with the SCB content.

regard to Ziegler-Natta catalysts since the latter need higher comonomer concentration in the reactor to reach such values of density, crystallinity and melting temperature.[24] That is, comonomer incorporation seems to be improved by the use heterogeneous metallocene catalyst in comparison to Ziegler-Natta catalysts.

Finally, data of Table 1 show that molecular weight of polymers decreases slightly when increasing temperature but it does not suffer important changes using different 1-butene initial concentration.

1-Butene incorporation was also studied by CRYSTAF analysis. It is based on the different temperature at which copolymer crystallizes from solution.[25] Figure 5 shows CRYSTAF results for copolymers obtained at 80 °C (from test 8 to 13). All the samples present unimodal composition distributions but a significant reduction of crystallization temperature is observed when increasing 1-butene fraction. These results are in agreement with others previously reported,[26,27] confirming the decrease of copolymers crystallinity with the comonomer incorporation. It is remarkable that low 1-butene contents in the copolymer (test 9 and 10) leads to CRYSTAF profiles slightly narrower than that corresponding to the homopolymer, suggesting that copolymers with very homogeneous distributions of 1-butene along polyethylene chains can be obtained when using this heterogeneous metallocene catalysts under the experimental conditions used. Increasing comonomer concentration in the reactor beyond 0.11 M (tests 11, 12 and 13) broadens the CRYSTAF curves. This trend could be related, at least in part, to the broadening of the distributions of ethylene sequence lengths between branching points.[26]

Conclusions

The ethylene polymerization in the presence of 1-butene using an heterogeneous zircocene catalyst (rac-Et(IndH$_4$)$_2$ZrCl$_2$ supported over silica/MAO) was investigated and the effects of comonomer concentration and reaction temperature were evaluated. Results obtained showed that an increase of the reaction temperature leads to higher catalytic activity and lower 1-butene incorporation. Changes of reactivity and diffusion coefficients of both monomers are suggested as possible causes of these trends. On the other side, 1-butene incorporation produces a beneficial effect on the activity related to the lower crystallinity of products obtained in presence of comonomer. This decrease of crystallinity

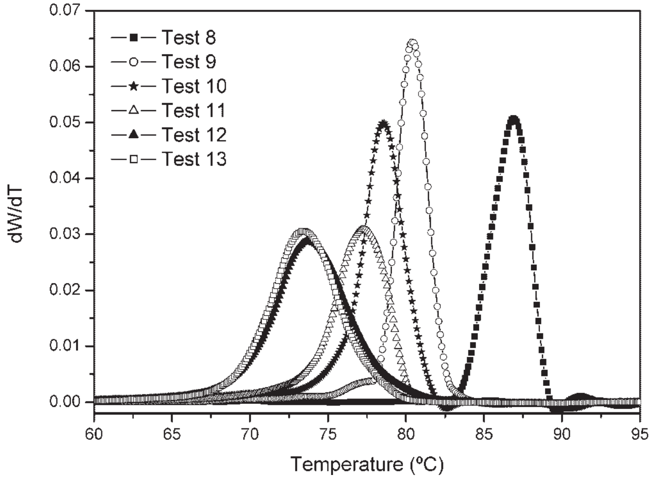

Figure 5.
CRYSTAF analysis of ethylene/1-butene copolymers obtained at 80 °C.

favours monomers diffusion through polymers shell formed during the reaction, dropping mass transfer limitations. Besides, others important changes of polymer properties were detected increasing 1-butene content. So, melting point and density of copolymers showed a linear decrease with increasing comonomer amount in the product, regardless of the reaction temperature. As well, a very small amount of 1-butene in the reactor leads to an important drop of these polymer properties indicating a good comonomer incorporation. CRYSTAF profiles displayed unimodal compositions distribution of copolymers. Also, at low 1-butene concentration, very narrow CRYSTAF profiles were observed confirming very homogeneous distributions of 1-butene along polyethylene chains.

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