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Effect of 1-Hexene Comonomer on Polyethylene Particle Growth and Kinetic Profiles

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Summary: The polymer growth and the microstructure of the final polymer are greatly affected by mass transfer, especially in the early stages of polymerization. In the present work, the catalytic system $(n\mathrm{BuCp})_2\mathrm{ZrCl}_2$/MAO immobilized over SiO_2-Al_2O_3 has been tested in ethylene-1-hexene copolymerizations using different amounts of comonomer. The catalytic activity shows a positive comonomer effect up to 1-hexene concentration of 0.724 mol/L since larger amounts of 1-hexene lead to a decrease in the activity. Copolymer properties analyzed by ^{13}C NMR, GPC, CRYSTAF and DSC point to the presence of important amorphous regions in the growing polymer chains as the 1-hexene concentration increases.
In order to study the incorporation of 1-hexene during ethylene polymerization, several experiments were performed with 0.194 mol/L of 1-hexene, 5 bar of ethylene pressure and different polymerization times. The incorporation of 1-hexene decreases slightly at polymerization times above 20 minutes. From cross-sectioned SEM images it can be concluded that the presence of 1-hexene helps catalyst fragmentation which could be related with the filter effect proposed by Fink.

Keywords: chemical composition distribution; comonomer effect; ethylene-1-hexene; supported metallocene catalysts

Introduction

Copolymers of ethylene with higher α–olefins such as 1-hexene, are very important commercial products classified as linear low density polyethylenes (LLDPE). The short branching coming from the incorporation of the α–olefins leads to lower melting points, crystallinities and densities, making films formed from these materials more flexible and better suited to process, finding applications in packing, shrink films or cable coatings, just to mention a few.[1]

On the other hand, enhancement of ethylene polymerization rate by α–olefin (comonomer) is a well-known phenomenon of considerable technological and scientist interest, called "comonomer" effect.[2,3] Several possible causes had been proposed to explain this fact, but the most supported[2–7] is the easier monomer diffusion due to crystallinity reduction of the growing polymer when a small amount of comonomer is added. In ethylene homopolymerization, the monomer diffusion is very slow through the highly crystalline polymer formed around the catalyst particle until sufficient polymer has formed to allow particle fragmentation. The comonomer addition leads to less crystalline polymer formation, which makes the diffusion of ethylene easier, and thus favors extended particle fragmentation.

Catalytic systems influence the structure and properties of the copolymer. Usually, Ziegler-Natta catalysts produce copolymers with a wide molecular weight distribution (MWD) and comonomer distribution (CCD) because of multiple active sites.[7–10] In contrast, homogeneous metallocenes are single-site catalysts and produce very

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uniform polymers with narrow MWDs and CCDs. However, these soluble metallocene catalytic systems are not suitable for their application on an industrial scale; gas-phase and slurry polymerization require the immobilization of metallocene catalysts on suitable carriers. This also helps to overcome other disadvantages such as low molecular weight and the lack of morphology of the polymers obtained with homogeneous metallocene catalysts.[11–14] There are several routes to support metallocenes[12] but it has been described that activating the metallocene with methylaluminoxane (MAO) in solution instead of carrying out the process with either the metallocene or the aluminoxane immobilized on the support, reduces the preparation time, maximizes the number of active centers and decreases the amount of solvent required for supporting.[14] To achieve an heterogeneous metallocene catalyst, inorganic materials such as silica, alumina, silica-alumina, magnesium chloride, clays, zeolites and mesoporous materials have been employed as carriers.[14,15]

An important aspect of olefin polymerization using heterogeneous catalysts, concerns the characteristics of polymer growth and catalyst particle fragmentation during the course of polymerization. As polymerization proceeds, the catalyst support becomes fragmented and dispersed within the growing polymer matrix and, therefore the morphology of the starting support is replicated in the final polymer. Various models describing particle growth during olefin polymerization have been developed.[16] The morphology of the polymer particle is a complex function of the polymer type, polymerization conditions, catalysts heterogeneization method and support properties as morphology and friability.[16,17] To provide true replication the catalyst particle must meet some requirements, summarized as follows[18]: (i) high surface area, (ii) high porosity, (iii) mechanical strength high enough to withstand mechanical processing, but low enough to allow the forces developed by the growing polymer to break down the initial catalyst particle into the microscopic particles that remain entrapped and dispersed in the expanding polymer, (iv) homogeneous distribution of the active centers and (v) free access of the monomers to the active centers.

When monomer contacts the active sites on the surface of the catalyst, polymer formation takes place and the fast-forming chains will be growing on the catalyst surface and pores, filling them up and leading to the support fragmentation. The monomer must diffuse through the boundary layer around the catalyst particle and through its pores to reach the active sites, where polymerization occurs.[16,17] In ethylene polymerization, it is frequently observed that polymer growth starts at and near the particle surface, leading to the formation of a shell of polyethylene around the catalyst particle. This involves the diffusion limitation, preventing free access of the monomer to active sites within the particle. Polymerization then takes place layer by layer, as the monomer gradually diffuses through the outer layers to the core.[4,18] This mechanism of particle growth is associated with a kinetic profile in which an initial induction period is followed by an acceleration period, after which, in the absence of chemical deactivation, a stationary rate is obtained.

As mentioned above, the addition of a comonomer such a 1-hexene changes the properties of the polymer layer around the catalyst particle which affects catalyst particle fragmentation and kinetic profiles. These monomer mass-transfer limitations can also contribute to compositional heterogeneity in the copolymer (broad CCD), even with metallocene catalysts.[4,6]

In this work we have investigated the synthesis of ethylene/1-hexene copolymers with $(nBuCp)_2ZrCl_2/MAO/SiO_2$-$Al_2O_3$ catalytic system, studying the influence of 1-hexene concentration on catalytic activity and polymer properties. From the analysis of kinetics profiles and ethylene/1-hexene copolymers obtained at various stages of polymerization, we determine the influence of polymerization time on activity and copolymers properties.

Experimental Part

Preparation of Supported Catalyst

Commercial silica-alumina with Si/Al = 4.8, supplied by Grace and calcined at 200 °C for 5 hours was used as support. Heterogeneous metallocene catalyst was prepared by impregnating the support with a solution of methylaluminoxane (MAO 30 wt% in toluene, Witco) and bis(butylcyclopentadienyl)zirconium dichloride ($(nBuCp)_2ZrCl_2$, Crompton) in dry toluene (99% wt, Scharlab). The impregnation was performed at room temperature, in a stirred vessel under inert nitrogen atmosphere during 3 hours. The amount of MAO and $(nBuCp)_2ZrCl_2$ was calculated in order to get supported catalyst with 15 wt% of Al and 0.3 wt% of Zr loadings. The volume of the impregnating solution was fixed as three-fold the pore volume of the employed support. Finally, the solid was dried under nitrogen flow and stored in glove-box as described previously.

Polymerization Reactions

Polymerizations were performed at 70 °C in a 1 litter stirred-glass reactor using tri-isobutylamunimum (TIBA, 30 wt% in heptane, Witco) as scavenger with an $Al_{(TIBA)}$/Zr molar ratio of 400. Ethylene (Air Liquide S.A., 99.99%) was deoxygenated and dried through columns containing R-3/15 BASF catalyst, alumina and 3 Å molecular sieve. The flow rate needed to keep a constant pressure of 5 bars during the reaction was measured by means of a mass-flow indicator (Bronkhorst Hi-Tec). Different amounts of 1-hexene (Scharlab, S. A., 97%) were injected into the reactor with a syringe at the beginning of the polymerization, where 600 cm^3 of n-heptane (Scharlab S. A., 99%) as solvent was added before. After the desired reaction time, the polymerization was stopped by depressurization and quenched by addition of acidified (HCl) methanol. Finally, the polymer obtained was separated by filtration and dried under atmospheric pressure at 70 °C.

Polymer Characterization

Molecular weight distributions were determined with a Waters ALLIANCE GPCV 2000 gel permeation chromatograph (GPC) equipped with a refractometer, a viscosimeter and three Styragel HT type columns (HT3, HT4 and HT6) with exclusion limit 1×10^7 for polystyrene. 1,2,4-Trichlorobenzene was used as solvent, at a flow rate of 1 cm^3 min^{-1}. The analyses were performed at 145 °C. The columns were calibrated with standard narrow molar mass distribution polystyrenes and with linear low density polyethylenes and polypropylenes.

Polymer melting points (T_m), crystallization temperatures (T_c) and crystallinities were determined in a METTLER TOLEDO DSC822 differential scanning calorimeter (DSC), using a heating rate of 10 $°Cmin^{-1}$ in the temperature range 23–160 °C. The heating cycle was performed twice, but only the results of the second scan are reported, because the former is influenced by the mechanical and thermal history of the samples.

Chemical composition distributions were measured by Crystaf (Polymer Char) using 1,2,4-trichlorobenzene as a solvent. Dissolution took place at 160 °C for 90 min followed by equilibration at 95 °C for 45 min. The crystallization rates were 0.1 °C/min from 95 to 19 °C. A two channel infrared detector was used to measure the concentration of polymer in the solution during crystallization.

A BRUKER AC300 spectrometer at 75 MHz was used to characterize the copolymers by ^{13}C NMR measurement and determine their 1-hexene molar fraction. The samples were added into sample tube with the mixture of 1,2,4-trichlorobenzene and 1,1,2,2-tetrachloroethylane-d_2 in a concentration of 10 vol%. Each sample was measured with 10 s pulse repetition.

Scanning electron micrographs were taken on a Phillips environmental scanning electron microscope XL30 ESEM equipped a tungsten filament and an accelerating voltage of 20 kV. For the fragmentation analysis the polymer particles were embedded in a low viscosity resin and cut with a razor blade.

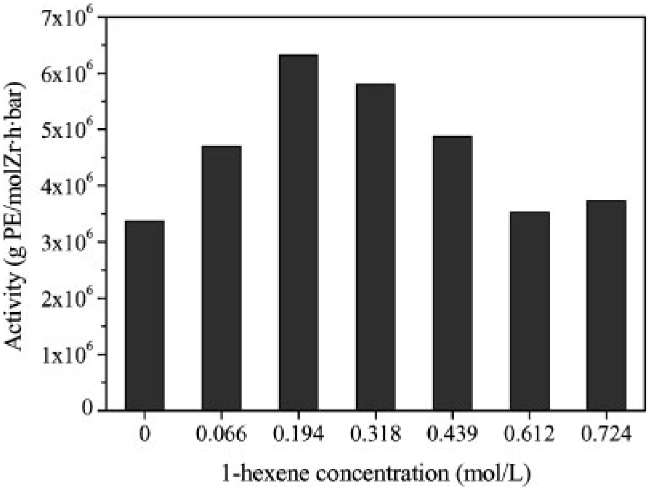

Figure 1.
Influence of the comonomer concentration on copolymerization activity using $(n\text{BuCp})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2\text{-Al}_2\text{O}_3$. Copolymerization reactions were performed as follows: Zr: 0.0020 mmol; 600 mL heptane; ethylene pressure: 5 bar; temperature: 70 °C; time: 30 minutes; TIBA was used as scavenger $\text{Al}_{(\text{TIBA})}/\text{Zr} = 400$.

Results and Discussion

The results of activity and polymers properties in the ethylene-1-hexene copolymerization using the heterogeneous $(n\text{BuCp})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalytic system are shown in Figure 1 and Table 1. It can be observed how polymerization activity first increases and then decreases with the increasing comonomer concentration, reaching maximum values at 0.194 mol/L. The initial enhancement in the catalyst activity is known as ‘‘comonomer effect’’ and may be related with easier monomer diffusion. A monomer diffusion limitation occurs when the monomer polymerization rate is high in comparison to the diffusion rate through the catalyst particle. This is often the case in ethylene homopolymerization when a highly crystalline polymer forms around the catalyst particle, altering the first stages of the polymerization reaction. The monomer diffuses very slowly through this crystalline mass up to a stage at which sufficient polymer has formed inside the catalyst particle to allow particle fragmentation. The addition of a small amount of a comonomer decreases the crystallinity (see Table 1) of the polymer envelope, thus enhancing activity.[6]

Table 1.
Characterization of ethylene/1-hexene copolymers.

1-hexene loaded in the reactor (mol/L)	1-hexene in the copolymer (mol%)$^{a)}$	M_w (g/mol)	M_w/M_n	T_m (°C)$^{b)}$	α (%)$^{b)}$
0	0.00	311812	2.94	136	64
0.066	0.90	190401	2.70	122	51
0.194	1.9	172887	2.92	118	43
0.318	3.09	172215	2.78	109	36
0.439	3.94	206266	2.62	104	30
0.612	4.31	195107	2.87	96	26
0.724	4.80	239615	3.09	94	24

a) From ^{13}C NMR analysis;
b) Melting temperatures and crystallinity values determined from DSC analysis.

At higher 1-hexene concentrations the polymerization activity decreases, this behavior has also been observed by several authors using supported metallocene catalysts[5,9,19], which might be associated with an increase of the comonomer fraction in the polymeric growing chain leading to a reduction in activity because of a decrease in the propagation rate with the comonomer concentration.[5,20]

As shown in Table 1, the incorporation of comonomer, determined by means of ^{13}C-NMR spectroscopy, increases with an increase in 1-hexene concentration in the polymerization reactor. The average molecular weights of ethylene/1-hexene copolymers are significantly lower than the one corresponding to the homopolymer, which is characteristic of metallocene based catalyst because the comonomer promotes chain termination [21,22]. However, the polydispersity index is independent of the comonomer content.

Figure 2 shows the kinetic profiles obtained for the copolymerization of ethylene with different amounts of 1-hexene in comparison with the results obtained in homopolymerization.

The kinetic profiles of ethylene consumption for comonomer concentrations in the range 0–0.439 mol/L, show an increase of the polymerization rate during the first 10 minutes of reaction and afterwards it remains constant at different ethylene flow rates. Nevertheless, at higher 1-hexene concentrations (0.612–0.724 mol/L) the profiles reach a maximum value at a reaction time around 15 minutes, probably due to the increase of the comonomer in the polymeric growing chain which might lead to a reduction in activity.[23]

Figure 3 shows the overlay of the CRYSTAF profiles of ethylene/1-hexene copolymers synthesized. The crystallization profiles broaden relative to the homopolymer with increasing comonomer content and consequently the amount of soluble fraction increases.[24,25] The peak crystallization temperatures decrease with increase in comonomer content as already observed on DSC analysis.

Fink et al.[4] ascribed the compositional distribution of ethylene/1-hexene copolymers prepared with a SiO_2/methylaluminoxane (MAO)/zirconocene system to the formation, during the initial stages of polymerization, of a copolymer envelope surrounding the catalyst center. The easier diffusion of the smaller monomer, ethylene, with respect to 1-hexene was proposed to

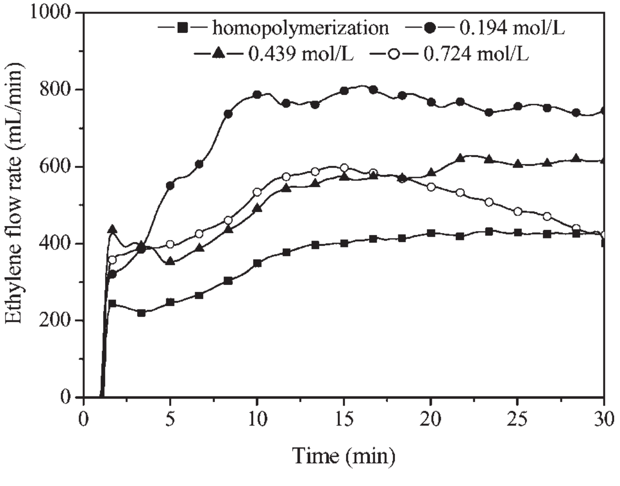

Figure 2.

Influence of the comonomer concentration on ethylene consumption during the copolymerization of ethylene/1-hexene using $(nBuCp)_2ZrCl_2/MAO/SiO_2\text{-}Al_2O_3$. Polymerization conditions: Zr: 0.0020 mmol; 600 mL heptane; ethylene pressure: 5 bar; temperature: 70 °C; TIBA was used as scavenger $Al_{(TIBA)}/Zr = 400$.

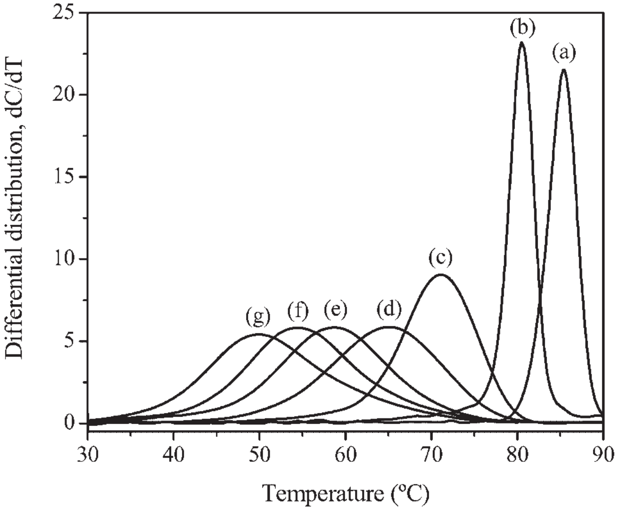

Figure 3.
CRYSTAF profiles of ethylene/1-hexene copolymers adding different concentrations (mol/L) of comonomer: (a) 0, (b) 0.066, (c) 0.194, (d) 0.318, (e) 0.439, (f) 0.612, (g) 0.724.

lead to a polymer particle comprising an ethylene-rich center and an outer layer formed by the copolymer, thus giving a broad overall chemical composition distribution. This phenomenon is termed as "filter effect".

In order to study the incorporation of 1-hexene during ethylene polymerization, several experiments were performed with 0.194 mol/L of 1-hexene, 5 bar of ethylene pressure and different polymerization times.

Figure 4 compares the activity values obtained in ethylene homo and copolymerization at different reaction times. It is possible to check that the presence of 1-hexene increases considerably the activity of the catalytic system reaching a maximum value at 20 min, while the homopolymerization

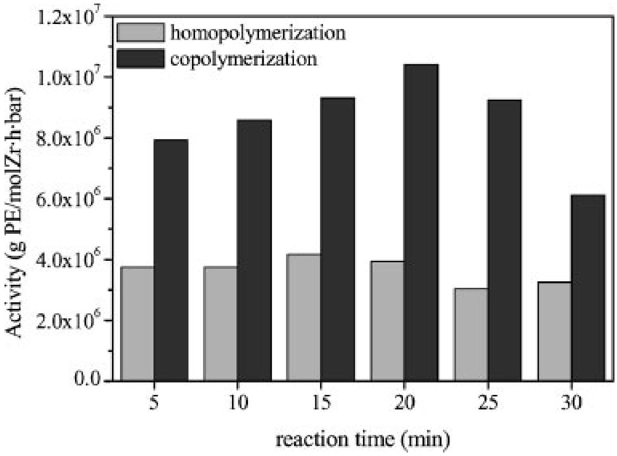

Figure 4.
Influence of reaction time on the catalytic activity in the homopolymerization and copolymerization of ethylene and 1-hexene (0.194 mol/L). Polymerization conditions: Zr: 0.0020 mmol; 600 mL heptane; ethylene pressure: 5 bar; temperature: 70 °C; TIBA was used as scavenger $Al_{(TIBA)}/Zr = 400$.

Table 2.
Characterization of homopolymers and copolymers obtained at different reaction times.

Time (min)	Copolymerization					Homopolymerization			
	1-hex. (mol%)[a]	M_w(g/mol)[b]	M_w/M_n[b]	T_m (°C)[c]	α (%)[c]	M_w(g/mol)[b]	M_w/M_n[b]	T_m (°C)[c]	α (%)[c]
5	2.1	290827	3.33	115	37	284120	3.08	135	60
10	2.1	224865	3.14	116	41	332498	3.34	133	62
15	2.1	184245	3.03	116	41	319972	3.13	133	62
20	2.1	173594	2.93	117	42	320933	3.33	134	62
25	1.9	161475	3.05	118	44	320638	3.19	134	63
30	1.9	172887	2.92	118	43	311812	2.94	136	64

[a] From ^{13}C NMR analysis;
[b] Melting temperatures and crystallinity values determined from DSC analysis.

activity remains almost constant with reaction time.

Table 2 shows the properties of homo and copolymers obtained. The percentages of 1-hexene in the copolymers revealed that after 20 minutes of polymerization time, the comonomer incorporation is slightly reduced. So, mass transfer limitations, which are less pronounced in the initial stages of polymerization, would result in better 1-hexene incorporation.[4]

No significant differences were found in the molecular weight of homo and copolymers obtained at different polymerization times.

As it was said above, the comonomer insertion decreases polymer melting temperature and crystallinity. In general, melting temperatures and the crystallinity of the copolymers increase with reaction time which corroborates the above mentioned Fink's filter effect, where in function of the reaction time the amount of polyethylene increases progressively in the copolymer.

Crystallization analysis fractionation (CRYSTAF) analyses of ethylene/1-hexene copolymers obtained at various stages of polymerization are shown in Figure 5. If 1-hexene is incorporated at the beginning of the reaction the copolymer chemical composition distribution will be broader (Figure 5, curves a) and b) with a maximum placed at lower temperatures respect to the homopolymer (Figure 3, curve a)), corresponding to 1-hexene rich fractions. In the filter effect theory, it is assumed that 1-hexene-rich polymer chains will form initially on the surface of the solid catalyst particle and that more rapid diffusion of the smaller ethylene monomer will subsequently result in a more polyethylene-rich core (Figure 5, curves d and e).

A further factor to be taken into account is the thermodynamic effects generated by the copolymer in the reaction medium, since increased ethylene sorption in the amorphous phase of the copolymer has been reported.[26,27] Moreover, the equilibrium sorption isotherms of ethylene/1-hexene

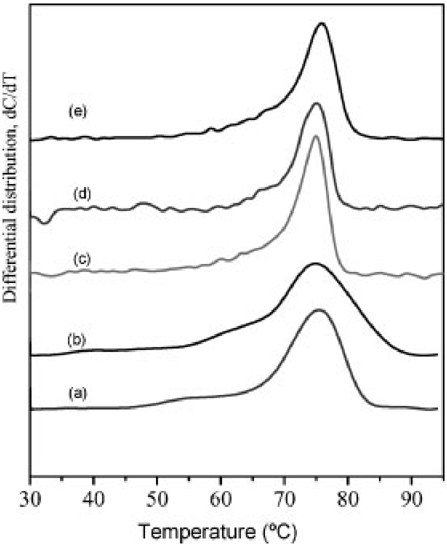

Figure 5.
CRYSTAF profiles of ethylene/1-hexene copolymers at different reaction times: (a) 5 minutes, (b) 10 minutes, (c) 15 minutes, (d) 20 minutes, (e) 25 minutes. 1-hexene concentration = 0.194 mol/L.

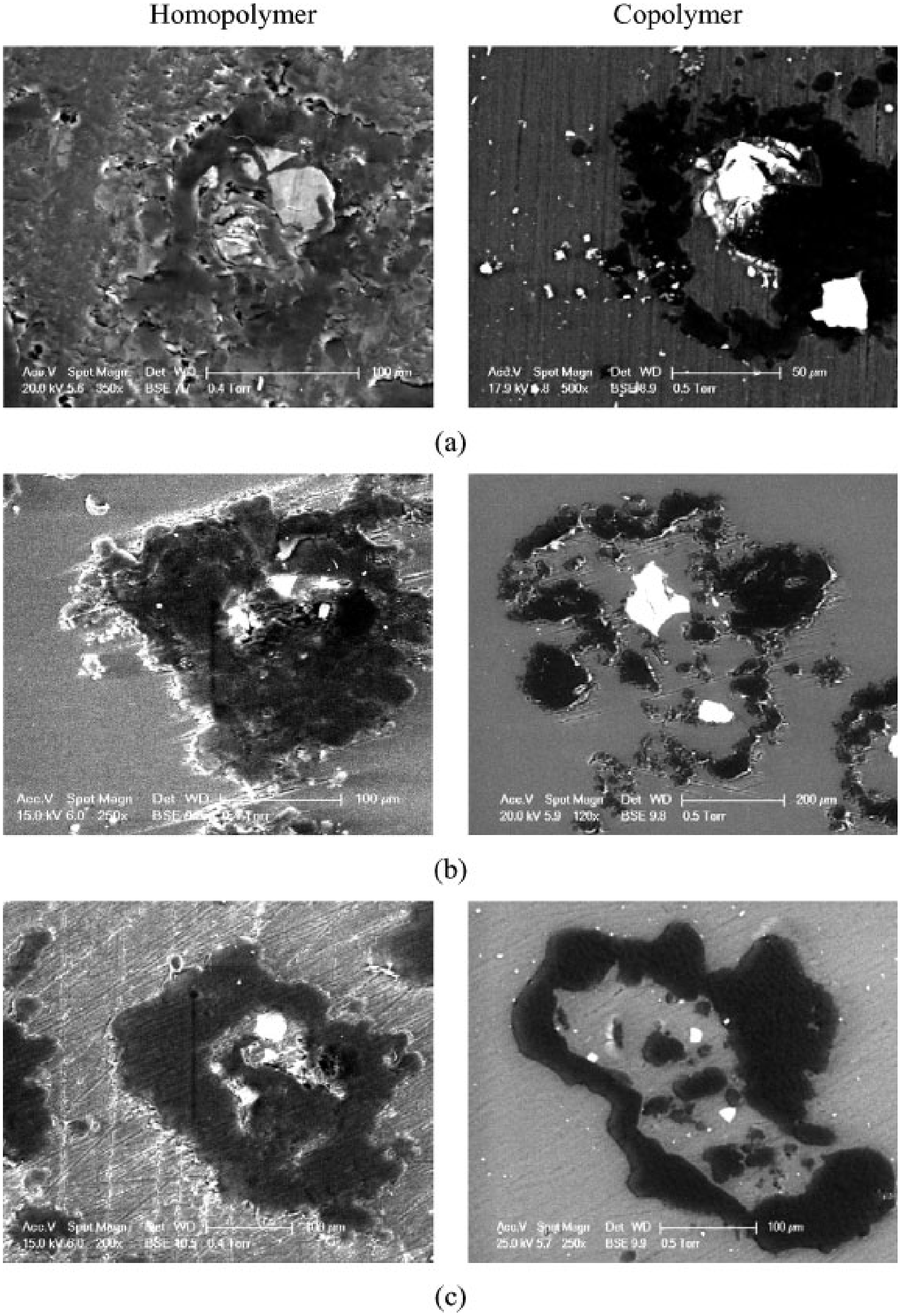

Figure 6.
Particle cross-sectional images of homopolymers and copolymers obtained at different reaction times: (a) 5, (b) 10 and (c) 20 minutes of polymerization.

mixtures in LLDPE show a cosolvent effect of 1-hexene in regards to ethylene that could contribute also to the increased polymerization activity.[28] On the contrary, the solubility of hexane is lower in the presence of ethylene, which could lead to a significant concentration profile of both olefins in the polymerization particles and therefore the widening of the crystaf profiles along the growth of the polymer particle.

The effect of comonomer incorporation on particle fragmentation during polymerization is illustrated in Figure 6 as comparison of homopolymers and copolymers at different reaction times.

In contrast to the incomplete fragmentation in the homopolymer, full fragmentation of the catalyst/support particle is obtained for ethylene/1-hexene copolymers.[6] That is, fragmentation during polymer particle growth is accelerated by the presence of 1-hexene as a comonomer. The formation of a polymer layer around a yet unfragmented core of the catalyst/support particle is clearly evident from cross-sectional SEM imaging of a particle obtained after 20 min of polymerization, as shown in Figure 6(c).

Conclusions

The activity of $(n\mathrm{BuCp})_2\mathrm{ZrCl}_2/\mathrm{MAO}/\mathrm{SiO}_2$-$\mathrm{Al}_2\mathrm{O}_3$ catalytic system in the 1-hexene/ethylene copolymerization increases with comonomer concentration up to 0.194 mol/L. The initial enhancement in the catalyst activity is related with better monomer diffusion. At higher concentrations of 1-hexene the activity decreases due to the lower insertion rate of the larger comonomer in the polymer chain.

The 1-hexene incorporation increases with the concentration in the polymerization reactor, obtaining ethylene/1-hexene copolymers with broader chemical composition distributions, lower molecular weights and crystallinity than ethylene homopolymer.

The percentages of 1-hexene in the copolymers obtained at different reaction times revealed that 1-hexene incorporation decreases at polymerization time above 20 minutes, because mass transfer limitations are less pronounced in the initial stages of polymerization. For this reason, the copolymer chemical composition distribution (CCD) during the first minutes of reaction is broader with a maximum placed at lower temperatures than homopolymer, corresponding to 1-hexene rich fractions. As polymerization time increases, the CCD curves become narrower with a maximum placed at higher temperatures as a result of the gradual formation of an ethylene-rich fraction in addition to the main copolymer fraction.

The presence of 1-hexene helps the fragmentation process, which could be related with the filter effect purposed by Fink in which it was proposed that the formation of an ethylene-rich fraction arises from easier diffusion of ethylene, with respect to 1-hexene, through a copolymer envelope formed in the outer regions of the catalyst particle. The changes in the sorption properties during the particle growing could lead to concentration gradients of both monomers which leads to the widening of the CRYSTAF profiles.

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