NOTE

Effects of Propylene Prepolymerization on Ethylene/1-Hexene and Ethylene/1-Octene Copolymerization with an Immobilized Metallocene Catalyst

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INTRODUCTION

It has been known for some time that the activity of a heterogeneous catalyst for ethylene polymerization can be increased if a prepolymerization is carried out first in the presence of propylene or another α-olefin.[1–5] Recently, it has been demonstrated that the increased polymerization activity can be attributed to a significant lowering of the monomer diffusion barrier in ethylene homopolymerization.[6]

The aforementioned studies were based on the use of $MgCl_2$-supported Ziegler–Natta catalysts. However, monomer diffusion limitation in ethylene polymerization is also a frequently encountered phenomenon in ethylene polymerization with immobilized single-center catalysts and provides the most likely explanation for the increase in activity when ethylene polymerization is carried out in the presence of an α-olefin comonomer.[7–11] The presence of the comonomer reduces the crystallinity of the polymer, leading to increased monomer sorption[12] and easier monomer mass transport through the growing polymer particle, and facilitates catalyst fragmentation. However, compositional heterogeneity in the resulting copolymer may still occur, even in the case of a single-center catalyst.[13–16] Fink et al.[14] 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 around the catalyst particle. Easier diffusion of the smaller monomer, ethylene, with respect to 1-hexene was proposed to lead to a polymer particle comprising an ethylene-rich center surrounded by an outer layer of the copolymer, thus giving a broad overall chemical composition distribution (CCD).

In recent ethylene/1-hexene copolymerization studies carried out with a catalyst comprising a zirconocene and MAO immobilized on a silica support, we found that the CCD of the copolymers became broader as the polymerization time was increased as a result of the gradual formation of a relatively high molecular weight, ethylene-rich fraction.[17] Again, this is a strong indication that significant monomer diffusion effects can play a role not only in ethylene homopolymerization but also in copolymerization. Taking into account that monomer diffusion effects may be reduced if a prepolymerization of the catalyst is carried out first with a

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Table 1. Effects of Propylene Prepolymerization on Ethylene Homo- and Copolymerizations

Propylene Prepolymerization	Main Polymerization	Activity (kg/mol of Zr h)	Comonomer Content in the Polymer (mol %)	M_w (g/mol)	M_w/M_n	Peak Melting Temperature (°C)
No	Ethylene	400	—	558,000	3.5	130.6
Yes	Ethylene	1,100	—[a]	278,000	4.8	127.6
No	Ethylene/1-hexene	600	5.2	326,000	3.8	85.3, 121.1
Yes	Ethylene/1-hexene	4,410	5.1[b]	271,300	4.9	94.3, 118.6
No	Ethylene/1-octene	600	2.0	361,000	3.7	93.1, 121.5
Yes	Ethylene/1-octene	2,000	1.0[c]	256,000	3.1	121.5

[a] This polymer contained 0.35 mol % propylene units because of the prepolymerization.
[b] The propylene units present in this polymer were below the detection limit.
[c] This polymer also contained 0.25 mol % propylene units.

monomer other than ethylene, we have now investigated the effects of propylene prepolymerization on ethylene/1-hexene and ethylene/1-octene copolymerization. Crystallization analysis fractionation (CRYSTAF) and differential scanning calorimetry (DSC) analysis of the resulting copolymers indicates that a significant narrowing of the composition distribution can indeed be achieved with this approach.

EXPERIMENTAL

Materials

All reactions were carried out under an argon atmosphere. A 10 wt % solution of MAO in toluene was obtained from Witco, whereas racemic ethylene-bridged bis(indenyl) zirconium dichloride [*rac*-Et(Ind)$_2$ZrCl$_2$] was purchased from Strem Chemicals. The silica support material, Sylopol 948, was kindly donated by Grace AG and calcined at 600 °C before use, as described previously.[18] Toluene (Biosolve) was dried on alumina columns, whereas *n*-heptane was distilled over potassium before use. Triisobutylaluminum (TIBA) was purchased from Akzo-Nobel as a 25 wt % solution in toluene. Ethylene (Air Liquide) was dried over columns containing an activated copper catalyst (BTS) and alumina before introduction into the polymerization reactor.

Catalyst Immobilization

Catalyst immobilization was carried out by 23.9 μmol of *rac*-Et(Ind)$_2$ZrCl$_2$ being brought into contact with 3.12 mmol of MAO (10 wt % in toluene) for 10 min, after which the resulting solution was slowly added to 1 g of silica in 1.5 mL of toluene at 0 °C. After a further 10 min, the temperature was gradually increased under reduced pressure to 63 °C over a period of 5 h to give a free-flowing powder.

Prepolymerization Procedure

n-Heptane (100 mL) was charged to a 1-L autoclave equipped with a hollow-shaft stirrer, and a propylene overpressure of 0.3 bar was applied for 30 min during stirring at 1000 rpm. The propylene line was then closed, and TIBA (1.8 mmol) was added, along with 75 mL of *n*-heptane, followed by the immobilized catalyst (250 mg) and a further 75 mL of *n*-heptane. The prepolymerization was carried out for 90 min at 50 °C.

Polymerization Procedure

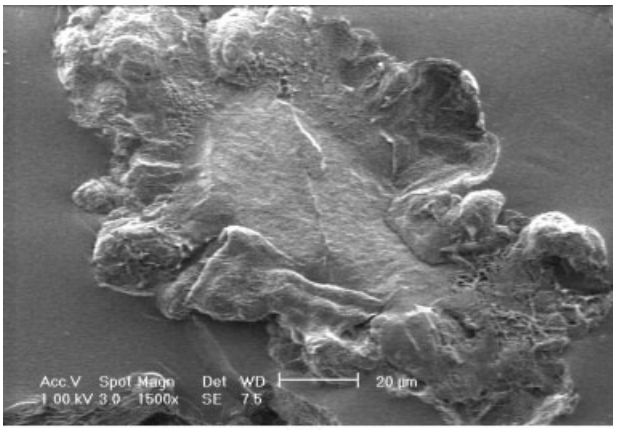
The copolymerization of ethylene and 1-hexene or 1-octene, following the aforementioned prepolymerization, was carried out by the charging of the desired amount of the comonomer to the reactor, along with *n*-heptane (300 mL), after which an ethylene pressure of 2.4 ± 0.1 bar was applied. After 1 h of polymerization at 50 °C, the reactor was degassed, and the slurry was quenched with acidic methanol. The polymer was dried *in vacuo* at 60 °C.

In experiments in which no prepolymerization with propylene was carried out, the autoclave was first charged with *n*-heptane (400 mL), and after it was heated to 50 °C, an ethylene monomer pressure of 2.4 ± 0.1 bar was applied. The reactor contents were stirred for 30 min at 1000 rpm to ensure maximum dissolution of the gaseous monomer. TIBA (1.8 mmol) was then added, along with the desired amount of the comonomer and 40 mL of *n*-heptane. After 15 min, the immobilized catalyst (250 mg) was charged to the reactor along with 22 mL of *n*-heptane. The polymerization was carried out for 1 h at 50 °C.

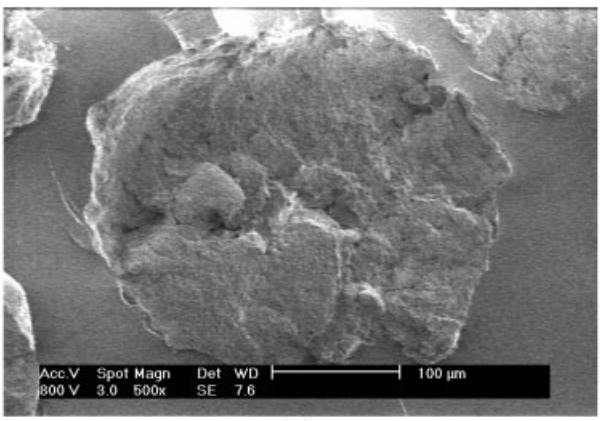
Polymer Characterization

High-temperature gel permeation chromatography was carried out in 1,2,4-trichlorobenzene at 140 °C with a GPC PL 220 from Polymer Laboratories with refractive-index detection. A column system consisting of five polystyrene columns (PSS SDV; 10^7, 10^6, 10^5, 10^3, and 100 Å) was used. Calibration using polystyrene standards was applied.

The copolymer CCD was measured by CRYSTAF with a model 200 from PolymerChar SA (Valencia). The



(a)



(b)

Figure 1. Cross-sectional SEM images of polyethylene particles prepared (a) without prepolymerization and (b) with propylene prepolymerization.

sample was dissolved at 160 °C in 1,2,4-trichlorobenzene, and the solution (concentration = 0.5 mg/mL) was stabilized at 100 °C and then cooled to 20 °C at 0.1 °C/min.

DSC was carried out with a Q100 differential scanning calorimeter (TA Instruments). The samples (1.5–2.5 mg) were heated to 160 °C at a rate of 10 °C/min and cooled at the same rate to −50 °C. A second heating cycle at 10 °C/min was used for data analysis.

Hexene and octene comonomer contents in selected polymers were determined by ^{13}C NMR (125.69 MHz) spectroscopy with a Varian Unity Inova 500 NMR spectrometer at 120 °C in 1,2,4-trichlorobenzene with deuterated tetrachloroethane as the lock solvent.

Scanning electron microscopy (SEM) characterization of the polymer particle morphology was carried out with a Philips XL-30 ESEM-FEG environmental scanning electron microscope. Secondary electron imaging of the sample surfaces was performed in a high-vacuum mode with an acceleration voltage of 1 kV. For particle cross-sectional analysis, polymer samples were embedded in a SPURR low-viscosity epoxy resin (SPI Supplies) and cut with a razor blade after cooling in liquid nitrogen.

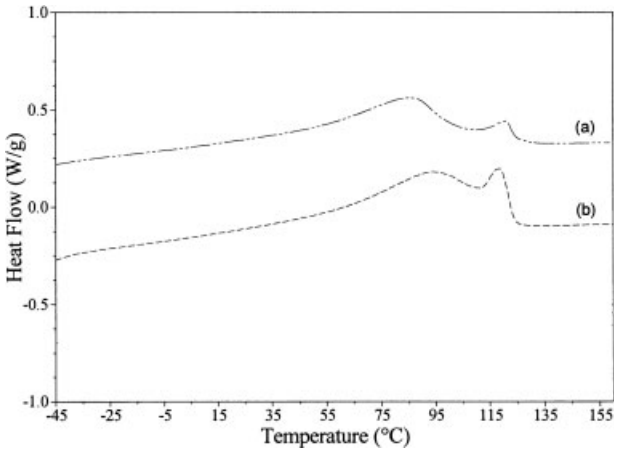


Figure 2. DSC thermograms of ethylene/1-hexene copolymers prepared (a) without prepolymerization and (b) with propylene prepolymerization.

RESULTS AND DISCUSSION

The catalyst used in this work was prepared by the impregnation of a silica support (Sylopol 948; precalcined at 600 °C) with a mixture of MAO and *rac*-$Et(Ind)_2ZrCl_2$, as described previously. The Zr and Al concentrations in the immobilized catalyst were 0.17 and 8.6 wt %, respectively.[17]

The effect of a prepolymerization with propylene was first investigated for ethylene homopolymerization. The results in Table 1 show that the application of a propylene prepolymerization resulted in a significant increase in activity in the subsequent ethylene poly-

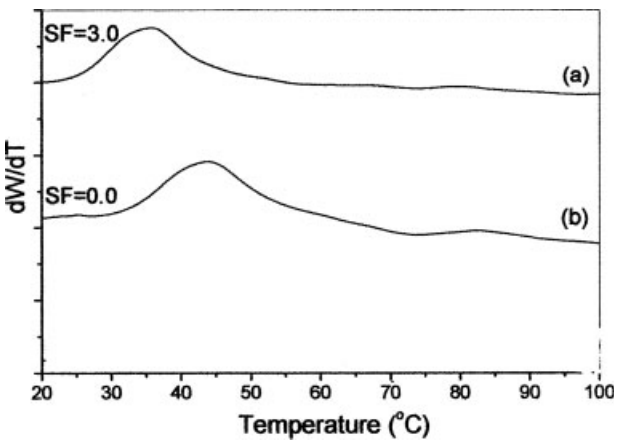


Figure 3. CRYSTAF analysis of ethylene/1-hexene copolymers prepared (a) without prepolymerization and (b) with propylene prepolymerization.

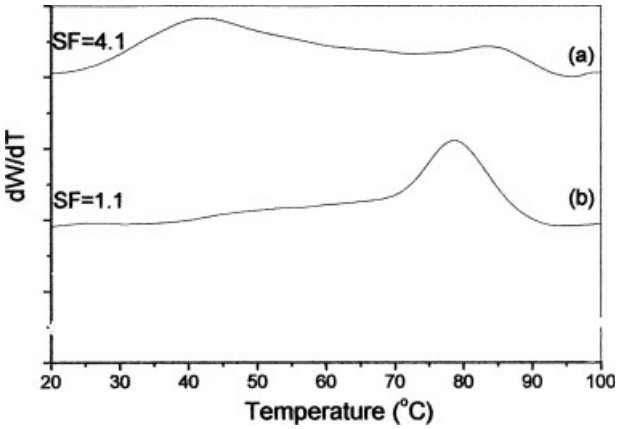


Figure 4. CRYSTAF analysis of ethylene/1-octene copolymers prepared (a) without prepolymerization and (b) with propylene prepolymerization.

merization. ^{13}C NMR analysis of the resulting polymer revealed the presence of 0.35 mol % propylene units resulting from the prepolymerization. The calculation of the actual amount of the polypropylene (PP) prepolymer produced revealed that this was only 27 mg. In other words, taking into account that the amount of the immobilized catalyst used was 250 mg, we found that the prepolymer yield was no more than 0.1 g of PP/g of catalyst. Furthermore, it is possible that not all the propylene present was consumed during the prepolymerization stage because DSC analysis gave a peak melting temperature of 127.6 °C, as opposed to 130.6 °C for the polyethylene prepared without prepolymerization. SEM of cross sections of polyethylene particles prepared without and with prepolymerization are shown in Figure 1(a,b), respectively. The presence of a polymer layer surrounding an unfragmented silica core was evident in the sample prepared without prepolymerization, whereas a uniform cross section indicative of complete fragmentation could be seen in the prepolymerized sample.

The data in Table 1 reveal very significant effects of a propylene prepolymerization on the activities obtained in ethylene/1-hexene and ethylene/1-octene copolymerizations. The comonomer (1-hexene or 1-octene)

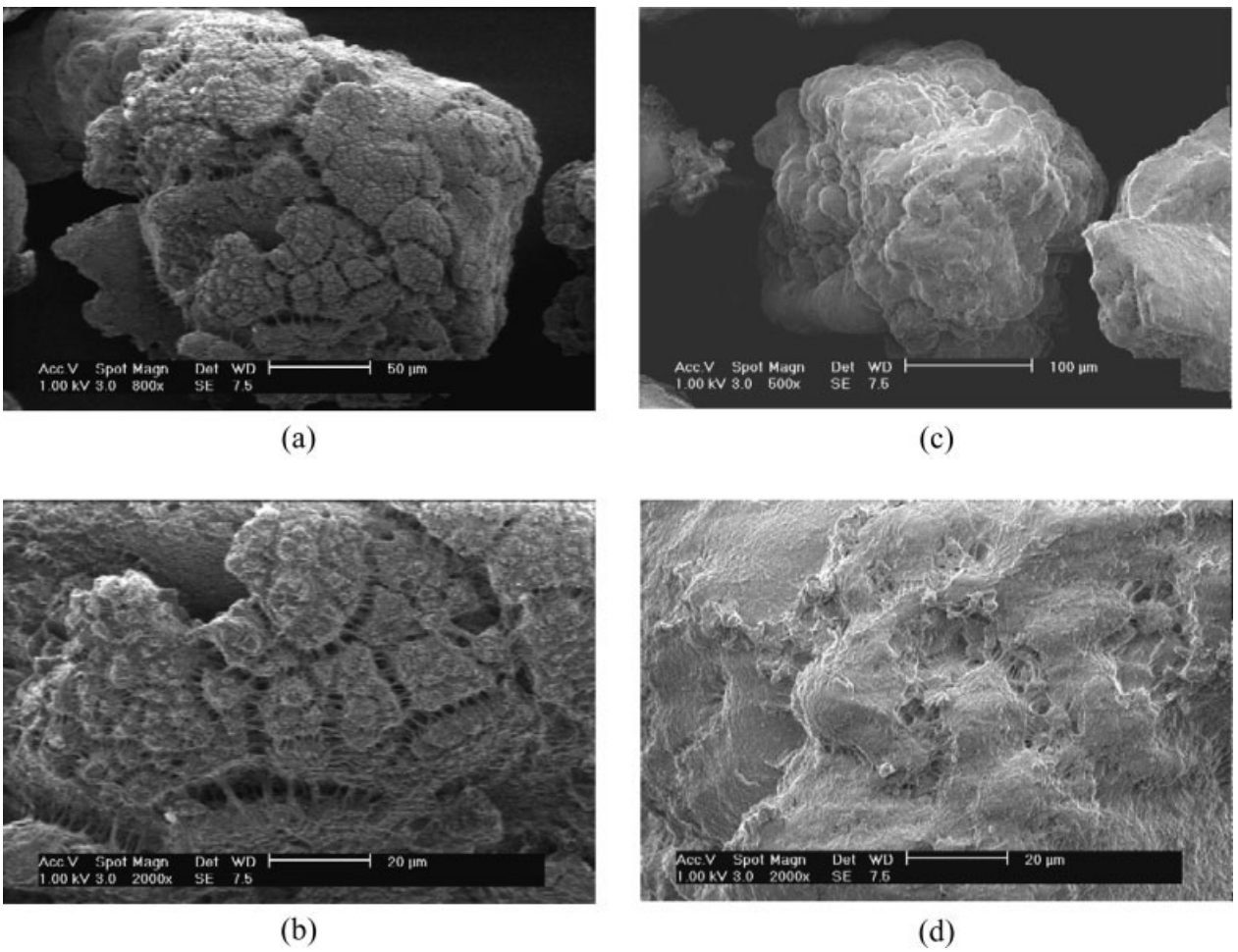


Figure 5. Particle morphology of ethylene/1-hexene copolymers obtained (a,b) without prepolymerization and (c,d) with propylene prepolymerization.

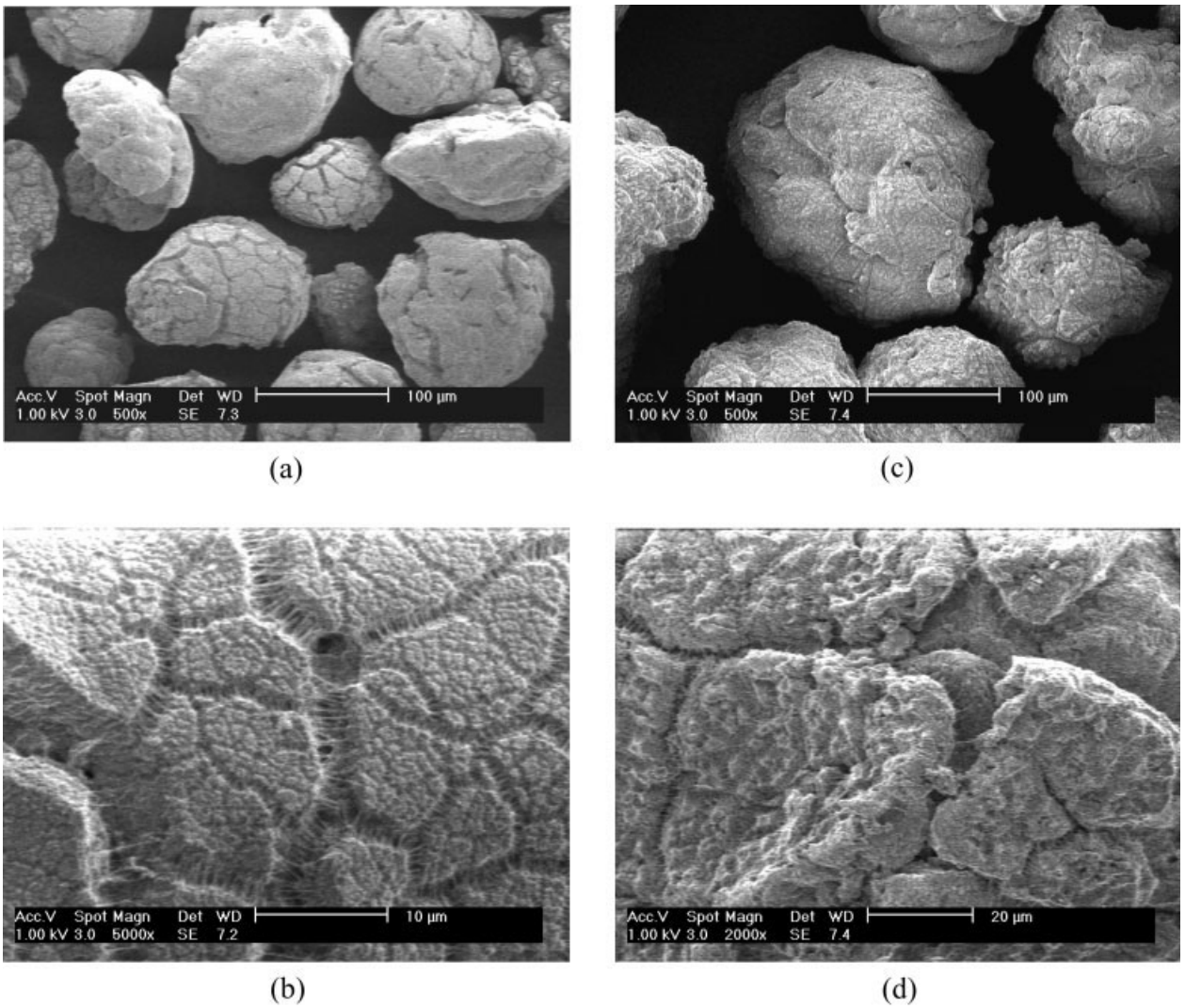


Figure 6. Particle morphology of ethylene/1-octene copolymers obtained (a,b) without prepolymerization and (c,d) with propylene prepolymerization.

concentration in these polymerizations was 0.17 mol/L. It is also evident that, as in the case of the ethylene homopolymerization, lower polymer molecular weights were obtained in the experiments in which a prepolymerization with propylene was carried out. This could be a result of the more complete fragmentation of the catalyst support following prepolymerization. In the case of ethylene homopolymerization, the lower molecular weight obtained with the prepolymerized catalyst could also arise from the presence of some unreacted propylene from the prepolymerization stage, taking into account the effect of α-olefin comonomers on chain transfer in ethylene polymerization.[19,20]

DSC thermograms of the ethylene/1-hexene copolymers prepared without and with prepolymerization are shown in Figure 2. In each case, two distinct melting peaks are apparent, which could be indicative of the presence of polymer fractions differing in the comonomer content. Such fractions could arise from more rapid diffusion of the smaller monomer, ethylene, through the growing particle, resulting in the hexene content in the polymer formed toward the center of the particle being lower than that in the fraction formed at or near the particle surface.[14,17] However, the difference in the melting temperatures between the two peaks is less in the case of the prepolymerized sample, suggesting a beneficial effect of propylene prepolymerization on copolymer homogeneity. In these polymerizations, only 1–15% of the comonomer present was actually consumed; the decrease in the comonomer concentration during the course of polymerization would therefore have only a limited effect on the compositional homogeneity of the resulting copolymers.

To investigate the effect of propylene prepolymerization on the copolymer CCD, CRYSTAF analysis was carried out on the ethylene/1-hexene and ethylene/1-

octene copolymers. This analysis technique makes use of the fact that the temperature at which an ethylene/α-olefin copolymer crystallizes from solution varies according to the comonomer content.[21] The CRYSTAF profiles of the ethylene/1-hexene and ethylene/1-octene copolymers prepared are shown in Figures 3 and 4, respectively. The soluble fraction (SF; %) for each polymer is also indicated, representing the proportion of the polymer remaining in solution after cooling to 20 °C. The decrease in SF, from 3.0 to 0% for the ethylene/1-hexene copolymers (Fig. 3) and from 4.1 to 1.1% for the ethylene/1-octene copolymers (Fig. 4), indicates a narrowing effect of propylene prepolymerization on the CCD of the copolymers. A significantly narrower CCD following prepolymerization is also apparent from the CRYSTAF profiles shown in Figure 4, in which a broad profile with two peak maxima is apparent for the nonprepolymerized sample. The high-temperature (ethylene-rich) fraction eluted at approximately 85 °C, as opposed to around 78 °C for the prepolymerized sample, even though the overall octene content in the latter was only 1 mol %, as opposed to 2 mol % for the nonprepolymerized sample. The CRYSTAF results therefore support the initial indication from DSC analysis that a more homogeneous comonomer distribution in ethylene/α-olefin copolymerization can be obtained when the catalyst is first subjected to a prepolymerization with propylene.

SEM images of ethylene/1-hexene and ethylene/1-octene copolymer particles obtained without and with prepolymerization are shown in Figures 5 and 6. In each case, prepolymerization with propylene is shown to have a notable effect on the particle surface, producing a more compact surface morphology than was obtained without prepolymerization, with less evidence of stretched fibrils. This, along with the beneficial effect of prepolymerization on particle fragmentation observed in ethylene homopolymerization, provides further evidence that diffusion limitations in both the homopolymerization and the copolymerization of ethylene can be somewhat alleviated if a prepolymerization with propylene is first carried out.

CONCLUSIONS

The prepolymerization of a silica-supported metallocene catalyst with propylene before ethylene/1-hexene or ethylene/1-octene copolymerization can lead not only to significant increases in the catalyst activity but also to a narrowing of the CCD in the resulting copolymers. It is proposed that this is the result of a more complete fragmentation of the support particle, reducing the effects of monomer diffusion limitations in ethylene copolymerization. These effects were observed at a very low (0.1 g of PP/g of catalyst) prepolymer yield. It is expected that further improvements in copolymer homogeneity could be achieved by more extensive prepolymerization.

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