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Synthesis and Characterization of Diolefin/Propylene Copolymers by Ziegler-Natta Polymerization

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Summary: Diolefins can be used as comonomers in propylene copolymerizations in order to modify some of the final properties of the obtained poly(propylene) (PP) resins. Although reduction of catalyst activity can be expected when such copolymerizations are performed with standard heterogeneous Ziegler- Natta catalysts, copolymers containing 1,5-hexadiene (HD) and 1,7-octadiene (OD) can be produced at high rates when the comonomer content is sufficiently low (below 2 mol%); however, the presence of very small amounts of 5-ethylidene-2-norbornene (ENB) leads to complete catalyst inhibition. It is shown that incorporation of dienes lead to decrease of the melting point of the final product, especially in presence of ENB. When compared to HD, addition of OD causes more pronounced modification of the melt flow index and weight-average molecular weight, although the xylene solubles is less sensitive to the comonomer feed when the comonomer composition is low. Obtained results indicate that small amounts of dienes can be used at plant site to modify the final properties of PP resins produced with standard heterogeneous Ziegler-Natta polymerizations.

Keywords: poly(propylene); 1,5-hexadiene; 1,7-octadiene; 5-ethylidene-2-norbornene; Ziegler-Natta polymerization

Introduction

Since the first appearance on the market, around 60 years ago, commercial polyolefin materials have gone through different development stages and achieved the current leadership on the plastic market in terms of both production volume and sales. Polyethylene (PE) and poly(propylene) (PP) markets represent about 67% of the worldwide demand for commercial thermoplastics, growing at annual rates that are close to 10%, fully justifying the continuous increase of investments in the field and the growing interest in the development of new polyolefin materials.[1] The versatility of available commercial polyolefin resins, coupled with the relatively low costs and very good processability of these materials, allow for development of several applications in many different sectors.[2] For instance, PP is widely used for manufacture of films, fibers, tubes, packing devices and materials, furniture, home appliances, internal and external automobile components, syringes, among many other things.[3] However, major drawbacks of isotactic PP are the reduced transparency and the low impact strength at low temperatures, near the glass transition temperature.[4,5]

A common strategy to modify the original properties of homopolymer resins is the incorporation of comonomers into the polymer backbone. The appropriate selection of comonomers allows for suitable modification of the original homopolymer structure and consequently of the end-use

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properties of the obtained copolymer material.[6–13]

The copolymerization of ethylene and propylene with dienes, including isoprene, 2-methyl-1,4-pentadiene, 2-methyl-1,5-hexadiene, 1,5-hexadiene, 7-methyl-1,6-octadiene, 1,7-octadiene and 1,9-decadiene, has been investigated by others, mainly with homogeneous catalyts. Particularly, zirconocene catalysts allow for efficient copolymerization and cyclocopolymerization of dienes, with predominat *trans* ring formation, although conservation of the double bond has also been reported. Analyses of the resulting copolymers indicated the decrease of molecular weight averages, melting temperature and cristallinity with the increase of the diene feed concentration.[7–13]

Surprisingly, very little is still known about the heterogeneous copolymerization of propylene with dienes, which are usually regarded as poisons of standard heterogeneous Ziegler-Natta catalysts and are not used commercially for production of copolymer PP grades.[14] A previous study regarding the slurry and bulk propylene polymerization performed in presence of 1-hexene and 1,5-hexadiene, using a commercial high activity heterogeneous Ziegler-Natta catalyst, showed that the density, characteristic transition temperatures, stiffness, average molecular weights and crystallinity of the obtained copolymers decreased in the presence of the comonomers. Incorporation of 1,5-hexadiene led to formation of cyclic structures and chain reticulation, while incorporation of 1-hexene led to formation of short branches.[6]

Based on the previous remarks, the main objective of the present study was the production of propylene copolymers with non-conjugated dienes (1,5-hexadiene, 1,7-octadiene and 5-ethylidene-2-norbornene), using a commercial third-generation Ziegler-Natta catalyst ($TiCl_4$ supported on $MgCl_2$), and the characterization of some fundamental parameters of the analyzed copolymerization systems. The effects caused by the incorporation of comonomers into the reaction system were evaluated in terms of the catalyst activity and in terms of the modification of some of the final properties of the obtained resins, characterized by ^{13}C Nuclear Magnetic Resonance (^{13}C-NMR), Differential Scanning Calorimetry (DSC), Gel Permeation Chromatography (GPC), Melt Flow Index (MFI) and Xylene Solubles (XS).

Experimental Part

Polymerization Reaction

The polymerization catalyst used in all experiments was a conventional commercial third-generation co-crystallized $TiCl_4$–$MgCl_2$ catalyst, provided as a powder and containing approximately 2wt% of Ti. Prior to use, the catalyst powder was suspended in a hexane solution containing the cocatalyst triethylaluminum (TEA) (15% m/m in hexane, provided by Albemarle) and the external electron donor cyclohexyl-methyl-dimethoxy-silane (donor C, with purity of 99.5%, provided by Degussa) for 10 minutes at room temperature. In all cases, the catalyst concentration was kept equal to 2.5 mg/l, the Al/Ti molar ratio was kept equal to 1500 and the Al/donor C molar ratio was kept equal to 20 (in accordance with previous experimental analyses). In case of copolymerizations, the diene comonomer was also added to this pre-contact mixture. All manipulations with air- and water-sensitive compounds were performed under dry nitrogen, using glove box and standard Schlenk techniques.

Polymerization reactions were carried out in a standard 4-l stainless-steel reactor, equipped with internal coils for refrigeration and temperature control. The reaction mixture was stirred continuously with a speed-controlled stirrer, equipped with a three-blade turbine impeller. Heat was provided by an external heating-mantle using steam. Reactor temperature and pressure were monitored and controlled in-line. Before feeding of chemicals, the reactor was blown with nitrogen (high purity polymerization grade provided by White Martins) to remove oxygen and humidity. The reactor was then charged with the pre-contact mixture, followed by 2.3 l of pressurized liquid propylene at 30 bar (high purity polymerization grade provided by White Martins). Reaction runs were conducted at 70 °C for 1 hour, under stirring of 500 RPM. Reaction runs were halted after reaching the specified batch time through reactor depressurization. The reactor was then cooled down to ambient temperature. The obtained polymer samples were dried in an oven with air circulation at 60 °C for 24 hours. Finally, the polymer powder was weighed and characterized.

Polymer Characterization

The molecular structure of copolymer samples was analyzed by ^{13}C-NMR. Samples were dissolved in 1,1,2,2-tetrachloroethane-d_2 (6.25 wt.%) and measurements were carried out at 120 °C. The spectrum was recorded and measured on a Varian Wide Bore 400 Spectrometer, operating at 100 MHz, in pulse Fourier transform mode. The results were assigned in accordance with the literature.[7,8,11–13,15,16]

DSC analyses (Perkin-Elmer DSC7 instrument, ranging from −20 °C to 200 °C at a scanning speed of 10 °C/min) were used to determine the characteristic transition temperatures and the heat capacities of the obtained polymer samples.[16] Sample holders contained about 20 mg of the analyzed resin. As usual, the first heating scan was discarded to eliminate the thermal history of the material, so that the reported values were measured during the second heating scan.

The MFI was determined in accordance with the ASTM D1238-95 procedure on a Tinius Olsen MP 993 instrument at 230 °C during 10 minutes. Variation of the resin flow rates with time can be observed due to viscous effects or polymer degradation, requiring tight control of the characterization time. The elastic effects are usually more pronounced with smaller MFI values.[18,19]

GPC analyses were performed to determine the Molecular Weight Distribution (MWD) and, therefore, the weight-average molecular weight (M_w) and polydispersity (PDI) of the obtained resins.[20] GPC analyses were performed in a Waters-150C chromatographer, equipped with a refractometric detector. Polymer samples were first dissolved in 1,2,4-trichlorobenzene; after 1 hour, samples were filtrated and injected into three Waters Styragel HT-6E columns under a flow rate of 1 ml/min. Measurements were performed at 140 °C. Polystyrene standards from Polymer were used to calibrate the GPC.

The XS content can be used to characterize the crystalline and amorphous fractions of the final polymer material. The XS usually comprises the atactic chains and oligomers, while the isotactic portion of the resin remains in the insoluble phase. XS analyses were performed in accordance with the ASTM D5492 procedure.

Results and Discussion

Figure 1 shows how the catalyst activity changes when the comonomer feed content increases. One can observe that the catalyst activity decreases with the increase of the comonomer content, being less pronounced for HD and more pronounced for ENB (as one might already expect, given the lower molar mass of HD and the larger molar mass of ENB). The catalyst activity is more sensitive to OD than to HD, suggesting that reactivity ratios for diene/propylene copolymerizations follow the well-known trends observed for α-olefin/propylene copolymerizations.[6–15] It is important to observe that reaction rates are still very high when 0.5 mol% of OD and 2 mol% of HD are present in the feed stream, which can be sufficient for significant modification of some of the polymer properties; however, reaction rates drop dramatically in presence of small amounts (2.5 mol%) of ENB resulting in the low activity of 0.4 Kg pol/g cat/h, probably preventing the use of ENB at plant site.

Figure 2 shows the expanded ^{13}C-NMR spectra of copolymer samples in the range between 10 and 55 ppm, obtained when the monomer feed contained 2 mol% of diene.

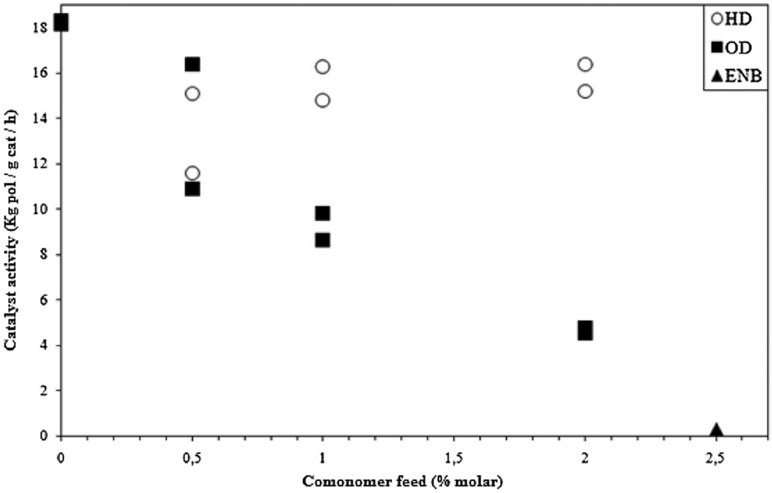

Figure 1.
Catalyst activity vs. *Comonomer feed composition* for copolymerizations performed with 1,5-hexadiene (○), 1,7-octadiene (■) and 5-ethylidene-2-norbornene (▲).

The broad signal range in the 31-45 ppm region is characteristic of intramolecular cycloaddition of nonconjugated dienes: cyclopentane for 1,5-hexadiene and cycloheptane for 1,7-octadiene.[7,8,11–13,15–16] The cyclic bond signal showed low intensity because the reactivity ratios in propylene/diene polymerizations favor the incorporation of propylene, so that the instantaneous diene composition of the produced copolymer is about 5 times smaller than the feed diene composition (explaining the low intensity of the ^{13}C-NMR signals for the comonomer).[6,11] However, it is possible to observe that the catalyst was able to incorporate comonomer and form cycles, in accordance with previous results.[6] Furthermore, the characteristic peak related to the pendant double bond, in the range between 115 ppm and 140 ppm,[13,15] cannot be observed, as also reported previously.[6]

The characteristic transition temperatures of some of the copolymer samples are shown in Figure 3. The insertion of the comonomer into the polymer backbone perturbs the crystalline isotactic structure of PP, leading to lower melting and crystallization temperatures (as one might already expect), although modification of Tm is small for HD and comparable to experimental errors. Crystallization temperatures are more sensitive to the presence of comonomer than the melting point, although the thermal behavior of the products is not affected significantly by the presence of comonomer in the feed in the analyzed experimental range. Despite the low catalyst activity, the most pronounced drop of the melting temperature was observed when the feed contained 2 mol% of ENB, probably because of the large molecular volume of ENB, leading to larger perturbation of the original crystalline structure of PP.[6–9]

Figure 4 shows the MFI values of the obtained copolymers as functions of the comonomer feed content. It is interesting to observe that MFI values are larger for HD than for OD, despite the apparently higher reactivity of the diene of lower molar mass. However, it is also interesting to observe that MFI values are larger in presence of HD than for the homopolymer and that MFI values of copolymers prepared with OD are smaller than the MFI values of homopolymers, although the decrease of MFI in the presence of OD is more pronounced than the increase of MFI values in the presence of HD. This result suggests that the elastic effect promoted by

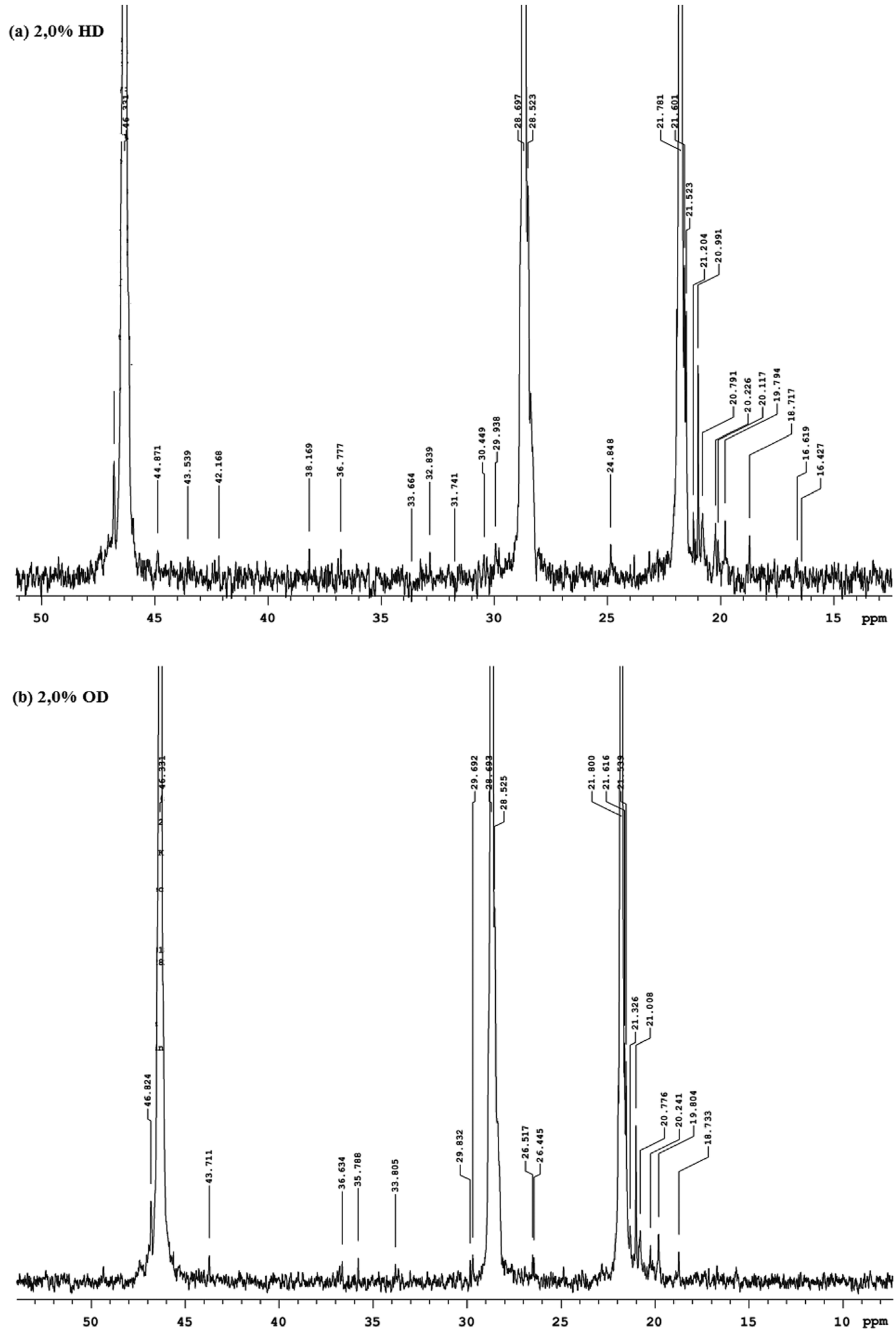

Figure 2.
^{13}C-NMR spectra for copolymer samples produced when the feed contained 2.0 mol% of 1,5-hexadiene (a) and 1,7-octadiene (b).

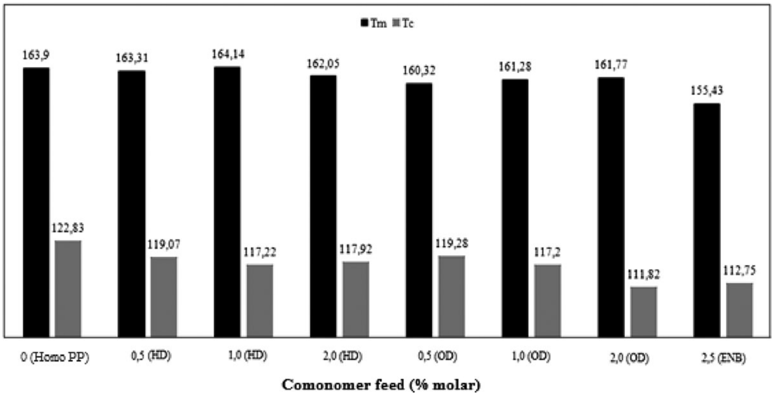

Figure 3.
Characteristic transition temperatures of the copolymer samples: ▬ melting temperature (T_m) and ▬ crystallization temperature (T_c).

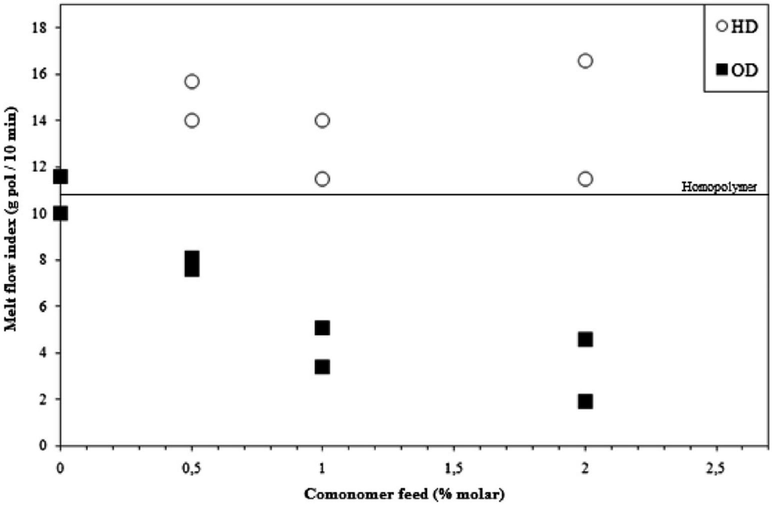

Figure 4.
MFI vs. *Comonomer feed composition* for copolymers produced with 1,5-hexadiene (○) and 1,7-octadiene (■).

the comonomer is more pronounced in the copolymers of higher molecular weight (OD copolymers), because the viscous polymer flow is normally more dependent on pressure when MFI values are smaller. This can also indicate the occurrence of more significant modification of the molecular structure, as in the case of formation of long branches. However, one must observe that the MFI is not a fundamental property, depending on different molecular parameters, including the molecular weight averages, copolymer composition and chain topology. Nevertheless, the MFI values provide evidences of incorporation of comonomer in the polypropylene chain.[18]

Figure 5 shows the weight-average molecular weights (M_w) of copolymer samples as functions of the comonomer feed composition. One can observe that obtained average molecular weights tend to increase with the comonomer feed composition in presence of either HD or OD, despite the higher MFI values of copolymer

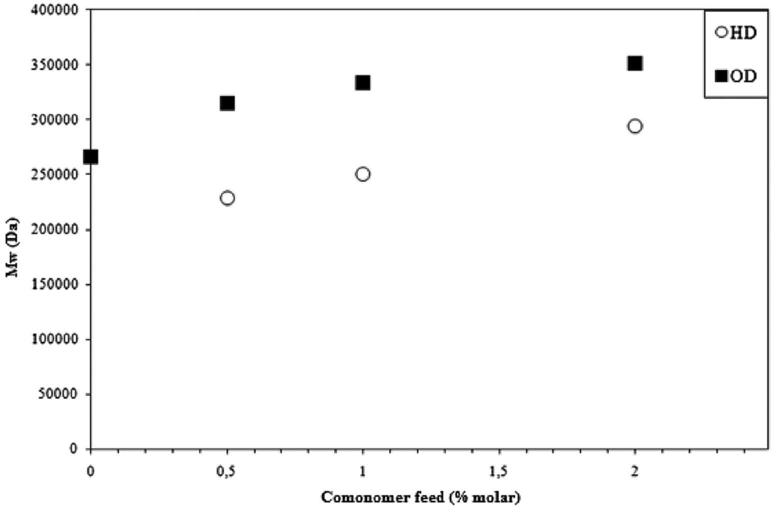

Figure 5.
Mw vs. *Comonomer feed composition* for copolymers containing 1,5-hexadiene (○) and 1,7-octadiene (■).

samples prepared in presence of HD. If Figures 4 and 5 are compared to each other, it becomes evident that the MFI values are controlled by M_w, although it is intriguing to observe that M_w values increase in presence of OD even with the lower catalyst activities. Again, this can indicate the occurrence of more significant modification of the molecular structure, as in the case of formation of long branches. M_w values of copolymers produced with HD also increased slightly, although the observed catalyst activity trend might suggest the opposite. The smaller changes of M_w in presence of HD can also indicate the higher reactivity of this diene, since the catalyst activity is less sensitive to the presence of HD than to the presence of OD.[7,8,12] This assumption is supported by independent NMR analyses, which indicate the higher incorporation of HD in propylene copolymerizations, when compared to OD.[6]

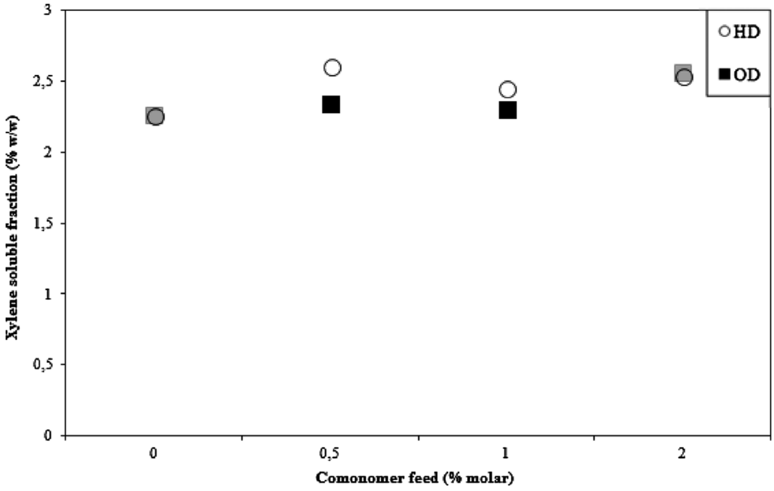

Figure 6.
XS vs. *Comonomer feed* composition for different copolymer samples.

Therefore, it seems that more complex structural molecular changes, including long chain branching, control the evolution of MFI and Mw values in the analyzed reaction system.

Figure 6 shows XS values for copolymers prepared at different conditions. In all cases, the presence of a comonomer in the feed stream leads to a slight increase of the XS values, as one might already expect.[6,13] However, the XS sensitivity to changes of the feed composition is very small, suggesting the low incorporation of comonomer in the final resin. Despite the low incorporation of comonomer, the results highlight the sensitivity of the weight-average molecular weights and MFI to small changes of dienes feed content.

Conclusion

It was shown that propylene copolymers containing 1,5-hexadiene (HD) and 1,7-octadiene (OD) can be prepared at high polymerization rates with a conventional Ziegler-Natta catalyst, provided that the comonomer feed content is sufficiently small (below 2 mol%). However, the presence of very small amounts of ethylidene norbornene (ENB) leads to severe catalyst inhibition. It was shown that catalyst activity tends to decrease, as the comonomer feed composition increases, although catalyst activity is more sensitive to presence of OD than to presence of HD. The characteristic transition temperatures and XS values are not very sensitive to the presence of comonomer in the feed, although addition of comonomers tends to shift the melting and crystallization temperatures to lower values and the XS values to higher values because of the formation of cyclic structures in the main chain. However, addition of HD and OD leads to significant changes of MFI values (which decrease significantly in presence of OD) and Mw values (which tend to increase in presence of both comonomers, despite the lower catalyst activities). This probably indicates the occurrence of more significant modification of the molecular structure, as in the case of formation of long branches.

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