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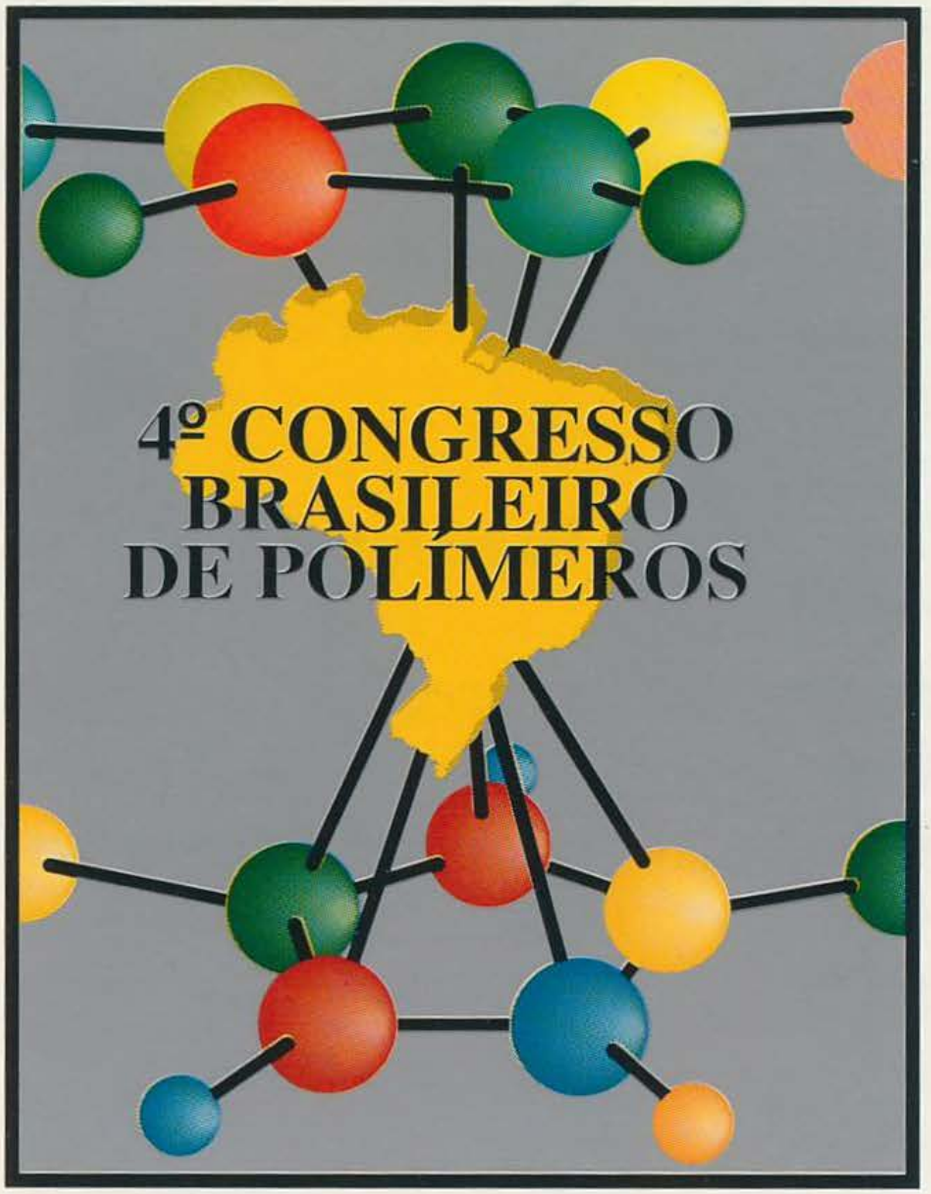

Promoção:

Associação Brasileira de Polímeros

COPOLYMERS OF ETHYLENE WITH LONG CHAIN α-OLEFINS USING A TYPICAL METALLOCENE CATALYST.

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ABSTRACT

The incorporation of a bulky group into a polyethylene chain has been studied. ^{13}C-NMR showed that 1-octadecene was incorporated into the main chain and the catalyst activity, and properties as melting point and crystallinity depend on comonomer concentration.

INTRODUCTION

One of the advantages of the homogeneous metallocene catalysts over the conventional Ziegler Natta catalyst is the ability to polymerize a wide variety of bulky monomers, such as higher α-olefins, styrenic compounds, dienes, cycloolefins and polar monomers. When bulky monomers are used in Ziegler-Natta catalysts the limiting factor is the very low reaction rate.

The advances in metallocene catalyst chemistry now offer a promising novel way not only to tailor polymer properties but also to produce entirely new polymeric materials. In the development of advanced technologies there will be an increasing demand for higher value-in use polyolefinic materials for special applications. Polyethylenes with higher α-olefins are important commercial products and consequently great efforts are made to find new and more efficient catalysts for comonomer incorporation.

The α-olefins copolymerizations using coordination catalysts has been of great interest already for some time , in order to reach branches of intermediate length. Long chain α-olefins are said to deactivate heterogeneous titanium catalyst but with catalysts, such as Cp_2ZrCl_2, $Et(Ind)_2ZrCl_2$, $Me_2Si(Ind)_2ZrCl_2$, and $iPr(FluCp)ZrCl_2$ the rate enhancement effect has been found [1-4].

The incorporation of bulky groups into polyolefins has been an area of interest in our research group, as it represents a useful method for modifying the properties of polyolefins. In this particular work we will present recent results coming from the copolymerization of ethylene with comonomer characterized for having long lateral branching as it is the 1- octadecene monomer using $EtInd_2ZrCl_2$/MAO as catalyst.

EXPERIMENTAL PART

Polymerization

All polymerization were conducted in an inert atmosphere. Toluene and 1-octadecene were refluxed and freshly distilled under argon from metallic Na. Polymerization-grade ethylene was dried by passage through 4 ▫ molecular sieve columns. $Et[Ind]_2ZrCl_2$ catalyst and methylaluminoxane (MAO) were obtained from Witco and used as received. All the polymerization were done in glass reactor at 60ºC for 30 minute and terminated by additions of

HCl/ methanol solution. The polymer was subsequently filtered, washed with methanol and dried in a vacuum.

Characterization of the polymers.

^{1}H and ^{13}C-NMR were employed to determined the composition of the copolymers. Differential scanning calorimetric (DSC) measurements were made with a Perkin Elmer DSC instrument. MW and MWD of the polymers were determined by a WATERS-150C GPC using universal calibration curve.

RESULTS

Results coming from ^{13}C-NMR and melting point proved the real incorporation of the long chain polyolefin on the polymer backbone. The catalyst activity show an increase with the comonomer concentration, this effect is a well known phenomenon for either Ziegler-Natta or metallocene catalysts. For this particular comonomer the catalytic activity is higher when compare with shorter chains as 1-octene. Table 1 shows the results for the incorporation of the comonomer and its influence on melting point and crystallinity. The values of crystallinity are lower than the values obtained for similar incorporation percentage when 1-hexene or 1-octene are used as comonomer. Further results will be presented during the Congress.

Table 1. Properties of ethylene/1-octadecene copolymers obtained with $EtInd_2ZrCl_2$/MAO catalyst system.T= 60ºC, Pressure= 0.6 bar, Al/Zr=1750.

Sample	Comonomer (ml)	Activity*	Incorporation (mol %)	T_m (ºC)]	ΔH_f (J/g)	Crystallinity (mol %)
AN-H21	0	18,400	0	131	163	56.2
AN-C11	5	24,000	1.15	120	108	40.0
AN-C21	10	36,000	2.0	115	103	36.0
AN-9C42	20	40,000	-	112	70	24.1

(* Kg PE/(mol Zr*bar*h))

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