



IX International Macromolecular
Colloquium

306628



6º CONGRESSO BRASILEIRO DE POLÍMEROS

IX INTERNATIONAL MACROMOLECULAR COLLOQUIUM

11 a 15 de novembro de 2001
Centro de Convenções do Hotel Serrano
Gramado/RS

Promoção:



Associação Brasileira de Polímeros

Instituto de Química da Universidade
Federal do Rio Grande do Sul (IQ/UFRGS)

MOLECULAR CHARACTERIZATION OF METALLOCENE ETHYLENE/CYCLOPENTADIENE AND ETHYLENE/DICYCLOPENTADIENE COPOLYMERS



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The effect of copolymerization temperature and amount of comonomer in the copolymerization of ethylene with 1,3-cyclopentadiene (CP) and dicyclopentadiene (DCP) using *rac*-Et[Ind]₂ZrCl₂/MAO metallocene system was studied. The amount of comonomer present in the reaction media influences the catalytic activity. In general, copolymers synthesized at 30 °C showed lower catalytic activities and higher comonomer incorporation. Ethylene/DCP (EDCP) copolymers with high comonomer contents (>9%) did not show melting temperatures. 1,3-cyclopentadiene dimerizes into dicyclopentadiene during the copolymerization giving a mixture of EDCP and ethylene/CP(ECP) copolymers. A complete characterization of the products was done by ¹H-NMR, ¹³C-NMR, HETCOR, DSC and GPC.

Introduction

The term polyethylene covers a wide range of ethylene based polymers with a variety of structures and properties. The discovery of new catalyst systems, such as the metallocenes in the early eighties, provided an unique opportunity to tailor-make new polymers and increased the range of comonomers that can be used.^{1,2} The introduction of functional groups in polyethylenes allows the preparation of new polymers and it may improve chemical and physical properties such as adhesion, dyeability, printability and compatibility with other polymers. This modification can be achieved mainly by three routes: a) Introduction of functional groups (maleic anhydride, acids, esters, etc.) using peroxides. b) Direct polymerization of olefins with functional groups.^{3,4} c) Copolymerization of α -olefins with dienes and consecutive conversion of the double bond into a polar group (epoxide, alcohol, etc.) which is an interesting route that can lead to polymers with defined and controlled structures.^{1,5} The use of dienes in copolymerization with α -olefins and terpolymerization is also of great industrial interest by itself.⁶ Ethylene-propylene-diene terpolymer (EPDM) is a synthetic rubber of great commercial importance.⁷ Dicyclopentadiene (DCP) has been widely used in industry to obtain the terpolymer EPDM,^{6,8} but its copolymerization behavior has been fairly studied academically. Dicyclopentadiene has been

terpolymerized with vanadium based Ziegler-Natta catalysts by the addition of the norbornene ring to the polymer backbone.⁷ Studies related to the copolymerization of ethylene with dicyclopentadiene were done with metallocenes (Cp₂ZrCl₂, Et[Ind]₂ZrCl₂ and Ph₂C(CpFluZrCl₂)) and using MAO as cocatalyst.⁵

The aim of this work is to give other insights on the copolymerization of ethylene with dicyclopentadiene and 1,3-cyclopentadiene using *rac*-Et[Ind]₂ZrCl₂/MAO and evaluate the properties of the copolymers obtained.

Experimental

Thermal Cracking of the Dicyclopentadiene

The dicyclopentadiene (DCP) is formed rapidly from 1,3-Cyclopentadiene upon storage. In order to obtain the pure CP monomer, it is necessary to thermally dissociate the dimer. By heating to 170°C, DCP dissociated to form two molecules of CP, which were distilled at 41.5 °C under argon and kept in a Schlenk flask at -10°C until being used in the copolymerization reactions.

Polymerization

The ethylene/cyclopentadiene copolymers were prepared using the *rac*-Et[Ind]₂ZrCl₂/MAO metallocene catalytic system. The polymerization reactions were carried out in a 1 L glass reactor equipped with a mechanical stirrer at one of three

different temperatures 30 °C, 40 °C or 60 °C. Toluene, MAO and the comonomer were added to the reactor under argon, the reaction medium was saturated with ethylene and the desired pressure was adjusted (1.6 bar). The reactions were initiated injecting the required amount of catalyst solution. After a total reaction time of 30 minutes, the polymer solution was poured into a HCl/methanol solution (1.5% v/v). The polymer was recovered by filtration, washed with ethanol and water and dried in vacuum until constant weight.

Characterization

The molecular weight of the copolymers was determined by gel permeation chromatography in a Waters 150 CV-plus System, equipped with an optic differential refractometer, a 150 C model, and a set of three columns, Styragel HT type (HT3, HT4, HT6) using an universal calibration curve for linear polyethylene, which was built with narrow molar mass polystyrene and polyethylene standards. The analyses were performed at 140°C and 1.0 mL/min, using 1,2,4-trichlorobenzene as solvent.

The composition of the ethylene copolymers was determined by ¹³C-NMR and ¹H-NMR. The ¹³C-NMR measurements were performed at 120°C with an acquisition time of 1.5 s, pulse width of 74° and pulse delay of 4 s on a VARIAN XL-300 spectrometer operating at 75 MHz. The samples were dissolved in o-dichlorobenzene and benzene-d₆ was used as an internal lock.

Differential Scanning Calorimetry (DSC) measurements were performed on a Polymer Laboratories DSC instrument under nitrogen atmosphere. Indium was used as standard. Samples were melted at 150°C, quenched from 150 °C to -20°C and heated from -20°C to 150°C at a heating rate of 10°C/min. The melting temperature (T_m) and the heat of fusion (ΔH_f) were taken from the second heating curve. The measured heat of fusion (ΔH_f) was converted to the degree of crystallinity (1-λ)_{ΔH} by taking 290 J/g as the enthalpy of fusion of a perfect polyethylene crystal.⁹

Results and Discussion

Dicyclopentadiene and 1,3-cyclopentadiene were copolymerized with ethylene at different comonomer concentrations and using three different temperatures. In general, the catalytic activities were higher at 60°C than at 30°C and 40°C for all copolymerizations as it can be seen for CP in Figure 1.

ECP and EDCP copolymers (figure 2) were studied by ¹³C-NMR and ¹H-NMR. The complete spectral assignment of ¹H-NMR spectra was done with the help of Heteronuclear Chemical Shift Correlation (HETCOR). ¹³C-NMR assignments were based on previous works.^{5, 7, 10} ¹³C-NMR spectra of EDCP and ECP copolymers were very similar, except for the fact that ECP copolymers showed some additional peaks which were not observed for EDCP (figure 3).

The same was observed regarding the ¹H-NMR spectra of both copolymers. The similarity in the spectra of ECP and EDCP copolymers suggests that the ECP copolymer was not a pure ethylene/cyclopentadiene copolymer, but a mixture of ethylene/dicyclopentadiene and ethylene/cyclopentadiene copolymers.

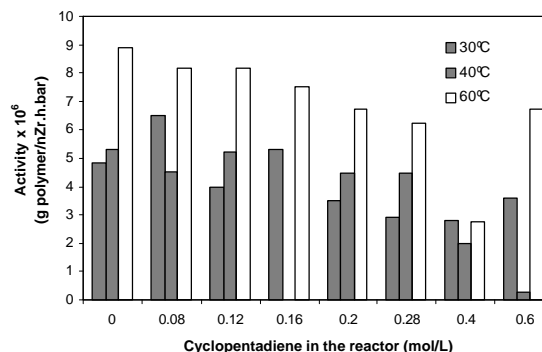


Figure 1- Catalytic activities of ECP copolymers at different temperatures and diene content in the reactor

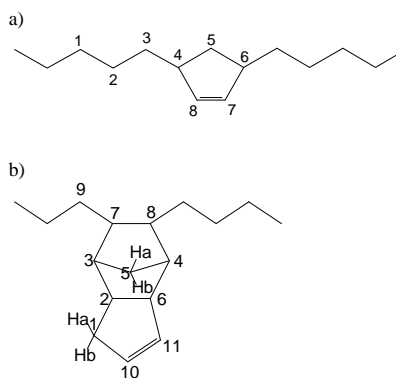


Figure 2- Schematic representation of (a)ECP; (b) EDCP copolymers

This conclusion comes from the fact that the comonomer CP easily dimerizes at room temperature. Considering that the conjugation of the double bonds makes this comonomer too stable to react rapidly with ethylene, and the dimerization is much faster, probably most of the CP dimerizes to give DCP prior to copolymerize with ethylene. In this sense, DCP is the comonomer that is incorporated with ethylene. A low amount of CP may incorporate in a 1,4-double bond addition to give the copolymer shown in figure 2(a). Through NMR analysis it was possible to calculate that only 20 to 30 % of the diene incorporated was due to the CP structure and at least 70 % was due to the DCP incorporation.

Fig 4 shows four ¹³C-NMR spectra of EDCP copolymers with different amounts of comonomer. It can be observed the presence of alternating sequences of DCP-E-DCP (peaks 4', 5', 7' and 8') for a copolymer with ~10 mol% of DCP. For other copolymers with DCP contents lower than 4.5 mol % there are only isolated units of DCP between ethylene

blocks. ^{13}C -NMR spectra of EDCP show that, in all cases, DCP incorporates to the ethylene chain with the *endo* configuration.⁷

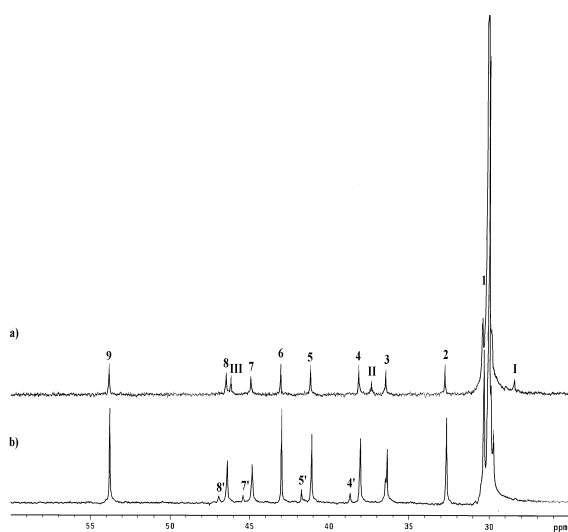


Figure 3 - ^{13}C -NMR spectra of (a) ECP ; (b) EDCP copolymers

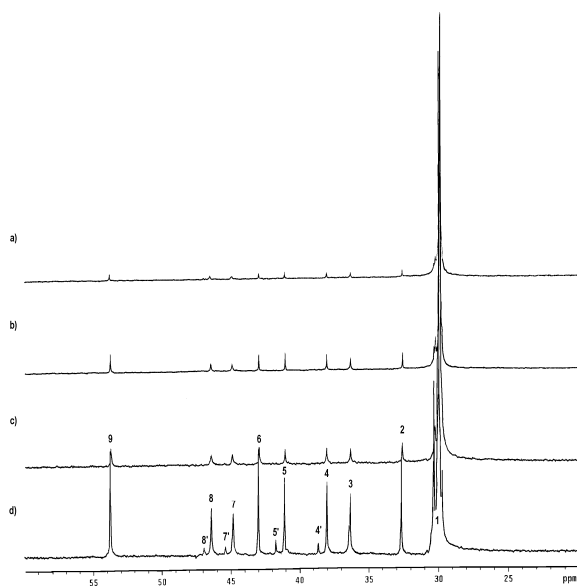


Figure 4- ^{13}C -NMR spectra of ethylene/dicyclopentadiene copolymers with different DCP contents: (a) 1.6 mol% ; (b) 3.3 mol% ; (c) 4.3 mol% ; (d) 9.7 mol%

Figure 5 shows the cyclodiene incorporation in the copolymer chain at different temperatures. As expected, the cyclodiene content in the copolymers increased with increasing the cyclodiene concentration in the reaction media. Incorporation of CP comonomer in copolymerization with ethylene was much lower than DCP incorporation, indicating that DCP is much more reactive than CP. The fact that CP dimerizes before the copolymerization was probably the reason for the lower catalytic activity and incorporation of this monomer if compared with DCP.

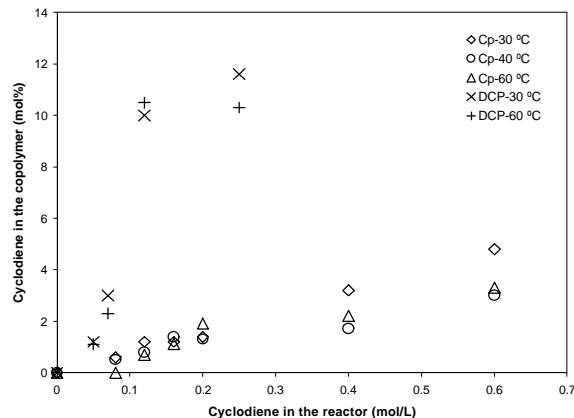


Figure 5- Cyclodiene content as a function of initial cyclodiene concentration in the reactor and copolymerization temperature.

Table 1 shows the molecular weight characterization and melting temperatures of the ECP and EDCP copolymers. It is well known that for random ethylene copolymers, as the comonomer content increases, the melting temperatures decrease due to the decreased number of crystallizable units. This general behavior was observed for all copolymers studied. Even though ECP and EDCP copolymers showed a decrease in the melting temperatures with the increase of comonomer content, the melting temperatures observed are higher than the ones usually observed for random ethylene/ α -olefins copolymers with similar comonomer contents.¹¹ The same was observed for the degree of crystallinity of these copolymers. This behavior was more remarkable at higher comonomer contents and it could be an evidence of a less homogeneous comonomer distribution.

It is known from the melting equilibrium theory of copolymers developed by Flory¹² that the melting temperature of a copolymer does not depend directly on its composition but rather on the nature of the sequence distribution. In the copolymers studied, less homogeneous intramolecular distribution could be caused by the differences in comonomer concentration in the reaction media during polymerization. The decrease of comonomer concentration with time would lead to differences on the comonomer distribution in the backbone. This fact has been already observed for ethylene/ α -olefin copolymers¹³ when the amount of comonomer in the reaction media was high.

One evidence of a non-homogeneous comonomer distribution was observed for ECP copolymers with high comonomer content (>3.3 mol%) which showed two melting temperatures. Considering that the melting temperature decreases with increasing comonomer content, one can conclude that the low temperature was related to segments of chain with high branch content and the higher temperature to segments of chain with lower amount of branches, or longer crystallizable sequences. In the case of EDCP copolymers, very broad endotherms

were observed as the comonomer content increases. When the amount of DCP comonomer was higher than 10 mol%, melting temperatures were not observed.

Conclusions

Catalytic activity was higher for DCP comonomer and all the comonomers showed better catalytic activities at 60°C. Incorporation of cycloienes was favored at 30°C but this difference was not sufficiently significant to compensate the lower catalytic activities obtained at this temperature. EDCP copolymers showed some [DED] triads for incorporations of DCP higher than 4.5 mol%. Most of 1,3-cyclopentadiene dimerized before the copolymerization with ethylene giving a product that was a mixture of ECP (20-30 mol%) and EDCP copolymers. Low decrease in the melting temperatures and crystallinity of most of the copolymers indicated a non-homogeneous distribution of the comonomer in the backbone.

Acknowledgements

The authors thank CAPES, CNPq and FAPERGS for the financial support and COPESUL, OPP Petroquímica and Witco for the supply of raw materials.

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Table 1 – Characterization of EDCP and ECp copolymers

Cyclic diene in the reactor (mol/L)	Polymerization Temperature														
	30°C					40°C					60°C				
	CP (mol%)	Tm (°C)	Xc (%)	Mw	Mw/Mn	CP (mol%)	Tm (°C)	Xc (%)	Mw	Mw/Mn	CP (mol%)	Tm (°C)	Xc (%)	Mw	Mw/Mn
0	0	131	58	155000	2.4	0	129	66	170000	3.0	0	129	59	194000	2.8
0.08	0.6	125	58	201000	2.5	0.5	123.7	42	169000	2.9	0.5	125	50	132000	2.7
0.12	1.2	122	47	182000	2.8	0.8	127	58	180000	3.2	0.7	124	53	125000	2.8
0.16	1.2	120	43	150000	2.8	1.4	113	38	129000	2.9	1.1	123	50	137000	2.8
0.20	1.4	122	47	153000	3.1	1.3	121.6	44	144000	3.3	1.9	123	53	147000	2.5
0.40	3.2	117/103	37	163000	3.1	1.7	120.7	41	127000	3.7	2.2	121	38	143000	2.5
0.60	4.8	113/89	30	177000	3.4	3	102	25	95000	3.0	3.3	120/92	34	118000	2.6
DCP	DCP (mol%)	Tm (°C)	Xc (%)	Mw	Mw/Mn						DCP (mol%)	Tm (°C)	Xc (%)	Mw	Mw/Mn
0.05	1.6	117	35	163000	2.6	-	-	-	-	-	1.1	123	39	n.d.	n.d.
0.07	3.3	105	24	143000	3.1	-	-	-	-	-	2.7	120.7	33	121000	3.2
0.12	4.3	117/87	21	135000	3.2	-	-	-	-	-	4.5	116.7	16	123000	3.2
0.24	9.7	n.o. ^a	-	n.d.	n.d.	-	-	-	-	-	8.2	106	8	n.d.	n.d.

(a) Tg= 14°C