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Preparation of Ziegler-Natta catalyst based on $TiCl_4$ modified with metal chlorides for copolymerization of ethylene and propene

Luiz Claudio de Santa Maria
Instituto de Ciências, Escola Federal de Engenharia de Itajubá, Av. BPS, 1303 PO Box 50, Itajubá/MG 37500-000, Brazil
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Copolymerizations of ethylene with propene were conducted in toluene employing the soluble catalytic system $TiCl_4.2THF/AlCl_2(C_2H_5)/Al(i\text{-}C_4H_9)_3$ combined with different metal chlorides ($CoCl_2$, $ZnCl_2$ or $MgCl_2$) complexed with tetrahydrofuran (THF). The catalyst activity was strongly dependent upon the metal chloride ($MtCl_2$) used as catalyst modifier and its Mt/Ti molar ratio. A clear increase of ethylene/propene copolymerization activity was noted up to Co/Ti and Mg/Ti = 2, after which it decreased markedly. The presence of $MtCl_2$ in the catalyst system had an important effect on the microstructure of copolymers.

(Keywords: Ziegler-Natta catalyst; ethylene/propene copolymerization; random copolymer)

Introduction

Poly(ethylene-*co*-propene), known as ethylene–propylene (EP) rubber, is an important elastomer. It is obtained industrially by vanadium catalysts such as VCl_4 and $VOCl_3$ activated with alkylaluminium chlorides, which are soluble in many hydrocarbon solvents[1,2]. These catalysts provide highly random copolymers from ethylene/propene polymerization, though their catalytic activities decrease markedly with temperature and time, particularly at high temperature[3].

Many kinds of heterogeneous titanium catalyst systems for ethylene and propene homopolymerization have been investigated. These catalyst systems have shown very high catalyst activity for ethylene and propene homopolymerizations; however, they give block copolymers of ethylene/propene instead of random ones, as obtained from vanadium catalysts[4,5].

In both systems, the trivalent species (Ti^{3+} and V^{3+}) seem to be active for ethylene and propene polymerizations. Makiro *et al.*[6] showed that soluble titanium compounds in hydrocarbon and/or halogenated hydrocarbon solvents could have an activity for random copolymerization of ethylene and propene higher than that of vanadium catalysts. On the other hand, Soga *et al.*[5] could obtain a moderately random copolymer of ethylene and propene with a heterogeneous catalyst based on SiO_2-supported $TiCl_4$. Generally, the formation of block copolymer is attributed to heterogeneity of catalyst species. Hence, if a homogeneous catalyst system in relation to catalyst sites is obtained, it is possible to control the production of random copolymer.

In order to clarify some doubtful points of ethylene/propene copolymerization, the influence of some metal chlorides on the catalyst performance was examined. Thus, preparative methods to synthesize a soluble $TiCl_4$ complex modified with $CoCl_2.2THF$, $MgCl_2.2THF$ or $ZnCl_2.2THF$ and their abilities for ethylene/propene copolymerization were studied (THF = tetrahydrofuran).

Experimental

Materials. Research grade ethylene, propene, THF and toluene were purified according to the usual procedures. Nitrogen of ultra-high purity (99.9989%, from Nippon Sanso Co.) was purified by passing through a 3 Å molecular sieve, P_2O_5 and $CaCl_2$ columns. The other chemicals (research grade) were purchased commercially and used without further purification.

EP copolymerization and analytical procedures. In a 100 cm^3 autoclave equipped with a magnetic stirrer were placed 20 cm^3 of toluene, 0.1 mmol of $TiCl_4.2THF$ and a given amount of $MtCl_2.2THF$ under nitrogen at room temperature. The mixture was then agitated for a certain time and a given amount of $AlCl_2(C_2H_5)$ was added at Al/THF = 1. The mixture was kept standing with vigorous stirring at room temperature, and after 10 min a certain amount of alkylaluminium employed as cocatalyst was introduced into the reactor. The reactor was cooled with liquid nitrogen, degassed *in vacuo*, and determined amounts of the purified monomers measured by a flowmeter were introduced. The polymerization was performed at 40°C for 15 min. The polymerization was terminated by adding dilute hydrochloric acid solution in methanol. The precipitated polymer was washed with methanol, followed by drying *in vacuo* at 60°C for 6 h. The ^{13}C n.m.r. spectra of the copolymers were recorded at 120°C using a Jeol FX-100 spectrometer in the pulse Fourier transform mode. The sample was made up in 1,2,4-trichlorobenzene/d_6-benzene (9/1 v/v) up to 20 wt%, using hexamethyldisilane (HMDS) as internal standard. The d.s.c. curves were obtained with a Shimadzu Thermal Analyzer DT-30 at a heating rate of 10°C min^{-1}. The electron spin resonance (e.s.r.) spectrum was taken in a Pyrex glass tube of 3 mm diameter at room temperature on a Jeol JES-RE-3X ESR spectrometer with 100×10^3 cycles/s field modulation. Mn(II) doped on MgO was used as standard to determine the g-values.

Results and discussion

Ever since the random copolymer of ethylene and propene was found to have interesting features, such as being an elastomer, catalysts for ethylene/propene copolymerization were investigated extensively with a new catalyst system. It is well known that vanadium catalysts, which produce V^{3+} species highly active for random EP copolymerization, are soluble in hydrocarbon solvents. On the other hand, conventional titanium catalysts are solid and insoluble in those solvents, and they have a low activity for random copolymerization despite their high activities for ethylene and propene homopolymerizations. Seemingly, if a Ti^{3+} species is soluble, it could have an activity for random EP copolymerization higher than that of vanadium catalysts. Thus, this work deals with a preparative method of synthesis of soluble Ti^{3+} compounds and their catalyst performances for EP copolymerization.

Recently, we have found that homogeneous catalyst systems composed of different kinds of titanium compounds modified with different additives are suitable for homo- and copolymerization of ethylene and propene[7–9] when activated by common trialkylaluminium compounds.

A type of catalyst for EP copolymerization was prepared, based on $TiCl_4.2THF$ modified with metal chlorides, which was shown to be soluble in the diluent of polymerization. It was previously found that propene and ethylene homopolymerizations could proceed with this catalyst system[9].

In a previous paper[9], it was noted that the $TiCl_4.2THF$ solubilized in toluene and activated with $Al(i\text{-}C_4H_9)_3$ (TIBA) was able to polymerize ethylene and propene only when $AlCl(C_2H_5)_2$, $Al_2Cl_3(C_2H_5)_3$ or $AlCl_2(C_2H_5)$ was employed as Lewis acid to form a soluble complex between the catalyst components under suitable conditions. Probably the ether had complexed the Ti catalytic species, consequently preventing the polymerization process. Among the alkyl chlorides employed as Lewis acids, ethylaluminium dichloride was judiciously chosen owing to its low reduction power in relation to other aluminium chlorides, thus avoiding the over-reduction of titanium species by the Lewis acid.

Table 1 shows the effect of metal chlorides on ethylene/propene copolymerization activity. With an increase in the Mg/Ti or Co/Ti molar ratios, the activity was enhanced to attain a maximum value at a molar ratio of about 2. At higher values of Mt/Ti molar ratio, the catalyst activity decreased: the excess THF may have poisoned the catalyst sites. The catalyst modified with zinc salt ($ZnCl_2.2THF$) was not active for EP copolymerization, as was verified for ethylene and propene homopolymerizations in an earlier paper[9]. The promotion of activity by using Co and Mg complexes could be attributed to the electronegativities of Mt^{2+} below 9.0 (Ti^{3+}), which affect the active sites and influence the electronic structure of the Ti^{3+} by inductive effects. The electron-donating capabilities of $MgCl_2$ and $CoCl_2$ to active titanium (Ti^{3+}) are likely either to stabilize the coordination of monomer with the active Ti(III) species or to activate the titanium–polymer bond[10].

Table 1 Results of ethylene–propene copolymerization[a]

Run	Catalyst system	Mt/Ti molar ratio[b]	Polymer yield (g)	T_m[c] (°C)
1	$TiCl_4.2THF$	0	0.30	120
2	$TiCl_4.2THF/CoCl_2.2THF$	1.0	0.50	118
3	$CoCl_2.2THF$	1.5	0.70	113
4	$CoCl_2.2THF$	2.0	1.25	–[d]
5	$CoCl_2.2THF$	2.5	0.63	118
6	$TiCl_4.2THF/MgCl_2.2THF$	1.5	0.65	119
7	$MgCl_2.2THF$	2.0	1.08	–[d]
8	$MgCl_2.2THF$	2.5	0.57	118
9	$TiCl_4.2THF/ZnCl_2.2THF$	1.0	trace	n.d.
10	$ZnCl_2.2THF$	2.0	trace	n.d.

n.d. not determined

[a] Copolymerization of ethylene and propene was carried out at 40°C in a stainless steel reactor for 15 min with 0.1 mmol of Ti in toluene (20 ml), using 0.5 mmol of TIBA as cocatalyst and ethylaluminium dichloride at Al/THF = 1, total amount of monomer = 8 l at normal conditions

[b] Mt, metal chloride (Co, Mg or Zn salts)

[c] From d.s.c. curve

[d] No peak of melting was observed

The EP copolymerization was carried out for a short time (15 min) to attain very low degrees of conversion (< 5%), such that the composition of comonomer feed is relatively unchanged from its initial value. Some analytical data of ethylene/propene copolymers are summarized in *Table 2*. Large differences between the catalysts were observed by the $S_{\alpha\beta}$ peaks, which are attributed to the chemical inversion of propene units of copolymer structure[2,4,11]. The catalysts modified with metal chlorides (Co and Mg salts) promoted chemical inversion, reaching chemical inversions as high as those obtained by vanadium catalysts. The microstructure of copolymers, shown in *Table 2*, was analysed by using ^{13}C n.m.r. spectra and the peak assignments were made according to the literature[12]. A typical spectrum of copolymer (run 4 in *Table 1*) produced with modified catalyst is shown in *Figure 1*. The copolymers obtained with catalysts modified at Mt/Ti higher than 2 presented a low content of propene units (polymers 5 and 8 in *Table 2*) and melting temperatures close to 120°C, indicating a long sequence of C_2H_5 units (see *Table 1*). The excess of ethylaluminium dichloride used to remove THF combined with TIBA could cause the over-reduction of Ti(III) to Ti(II), which is active only for ethylene.

By using the monomer sequence distributions in the copolymers, the products of reactivity ratio ($r_E r_P$) were estimated according to the literature[12,13]. As can be seen in *Table 2*, these products indicate that the copolymers obtained with modified catalyst are statistically random, whereas that obtained with the unmodified catalyst is poor in propene units and has a somewhat blocky character. In addition, the copolymers produced by modified catalysts at Mt/Ti = 1.5 (runs 3 and 6 in *Table 1*) are also poor in propene units and they are block copolymers.

To obtain a better insight into monomer sequence distributions in copolymer structures, the persistence

Table 2 Some analytical data of ethylene–propene copolymers

	Monomer content[b]		Dyad sequence distribution[b]					
Polymer[a]	[E]	[P]	[PP]	[EP]	[EE]	$r_E r_P$	ρ[c]	$[S_{\alpha\beta}]/[S_{\beta\beta}]$[b]
1	0.89	0.11	0.01	0.21	0.78	0.71	0.93	0.35
2	0.72	0.28	0.07	0.43	0.50	0.91	0.98	0.78
3	0.90	0.10	0.03	0.15	0.82	4.37	1.20	0.54
4	0.69	0.31	0.10	0.42	0.48	1.09	1.02	0.88
5	0.86	0.14	0.04	0.20	0.76	3.04	1.20	0.48
7	0.67	0.33	0.11	0.44	0.45	1.02	1.01	0.84
8	0.91	0.09	0.01	0.15	0.84	1.49	1.09	0.25

[a] Polymer number corresponds to run number in *Table 1*
[b] Estimated from ^{13}C n.m.r. spectra of the polymers
[c] Persistence ratio

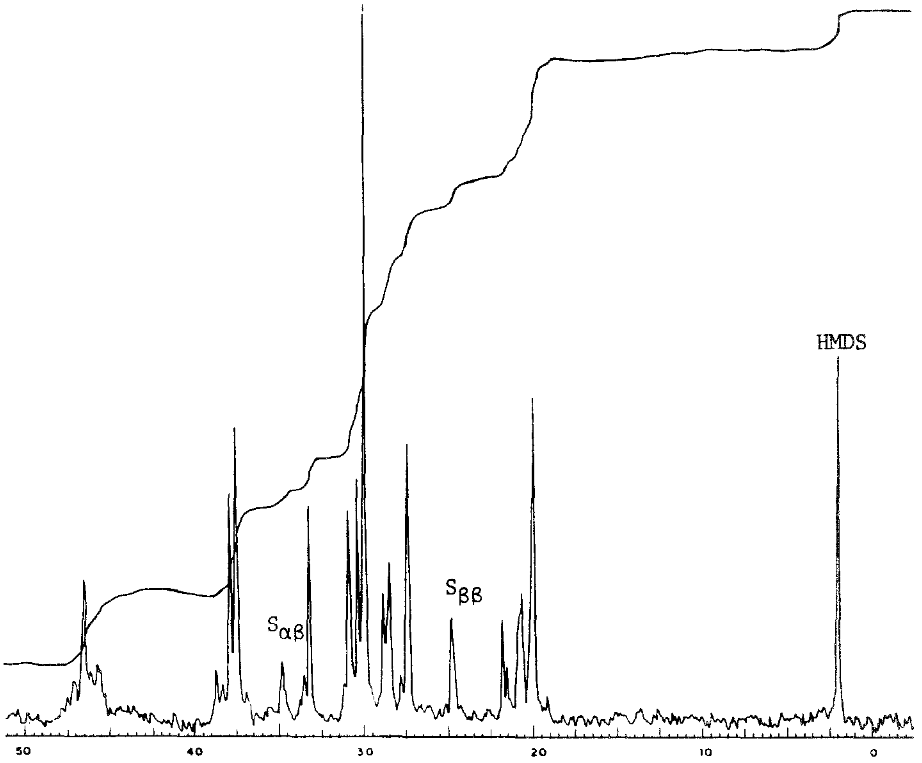

Figure 1 ^{13}C n.m.r. spectrum of ethylene–propene copolymer obtained by modified catalyst (run 4 in *Table 1*). Chemical shift assignments (in ppm) are from hexamethyldisilane (HMDS)

ratio (ρ) was estimated by using the following equation[14]:

$$\rho = 2[E][P]/[EP]$$

where [EP], [E] and [P] denote dyad sequence distribution and monomer contents in the copolymer. Persistence ratio (ρ) is defined as the actual mean length of the closed ethylene (or propene) sequence to the mean length of the Bernoullian process with the same ethylene (or propene) content. The persistence ratio of the copolymer (polymers 2, 4 and 7 in *Table 2*) was estimated to be very close to unity, confirming the conclusions above. These data indicate that the copolymerization proceeds according to Bernoullian statistics to give a random copolymer with these catalysts.

To reach a better understanding of this point, d.s.c. measurements were made. From the results in *Figure 2*, which shows curves of typical copolymers obtained with unmodified and modified catalyst, it can be observed that the copolymers presented different thermal outlines depending on the catalyst. The polymer produced by unmodified catalyst (curve A) displayed a clear peak at approximately 120°C, corresponding to the melting temperature of a long sequence of ethylene units. Some copolymers produced through modified catalysts displayed the melting temperature at lower values (curves B and C), showing that the sequence of ethylene units of copolymer chains became shorter than that shown in curve A. In addition, some copolymers produced with modified catalysts did not display any melting peak (curve D), again indicating a random distribution of ethylene and propene units in the copolymer chain. These results are in accordance with the data of ^{13}C n.m.r. discussed above.

It is well known that trivalent species of Ti(III) of conventional catalysts based on $TiCl_4$ are formed from the reaction between $TiCl_4$ and an alkylaluminium such as AlR_3 (R = alkyl group). Since the trivalent titanium has an unpaired electron in the 3d orbital, it is detectable

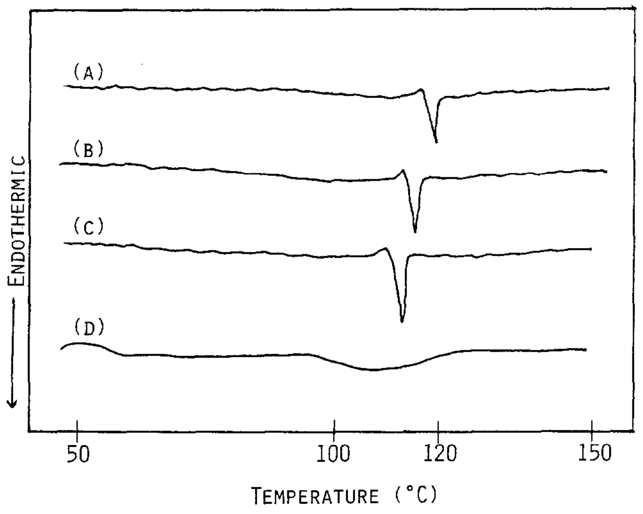

Figure 2 D.s.c. curves of ethylene–propene copolymers: A, obtained with unmodified catalyst (run 1 in *Table 1*); B and C, obtained with modified catalysts (runs 2 and 3 in *Table 1*, respectively); D, obtained with modified catalyst (run 4 in *Table 1*)

by means of e.s.r. measurements[15]. *Table 3* summarizes the spectral features of g-values of Ti(III) species obtained from different catalysts. It was noted that several g-values of Ti(III) species were displayed at Mt/Ti = 1.5 (runs 3 and 6), indicating heterogeneity of catalyst sites. These results can explain the differences found for the copolymers of runs 3 and 6 in *Tables 1* and *2*. In this case, maybe the heterogeneity of active species caused the formation of copolymers with poor contents of propene units, favouring the insertion of ethylene into the polymer chain. On the other hand, the catalyst prepared at Mt/Ti = 2.0 produced one signal in the e.s.r spectrum and the polymer obtained through this catalyst system presented a high content of propene units which were statistically distributed in the copolymer chain. Some e.s.r. spectra are shown in *Figure 3*.

Table 3 The g-values of the catalysts

Run[a]	g-value
1	1.9294
3	1.9156; 1.9191; 1.9246; 1.9314; 1.9336, 1.9405; 1.9523; 1.9582; 1.9622
4	1.9383
6	1.9163; 1.9314; 1.9410; 1.9505; 1.9621
7	1.9391

[a] Corresponds to run number in *Table 1*

The present results strongly suggest that there are two crucial points which have to be considered judiciously. The first is that the Ti(III) species are active for both monomers studied, while further reduced titanium species, which can be Ti(II), are active only for ethylene polymerization. The second is that a soluble system can produce random copolymers of ethylene and propene when Ti(III) species are homogeneously formed after reduction with alkylaluminium compounds at appropriate conditions.

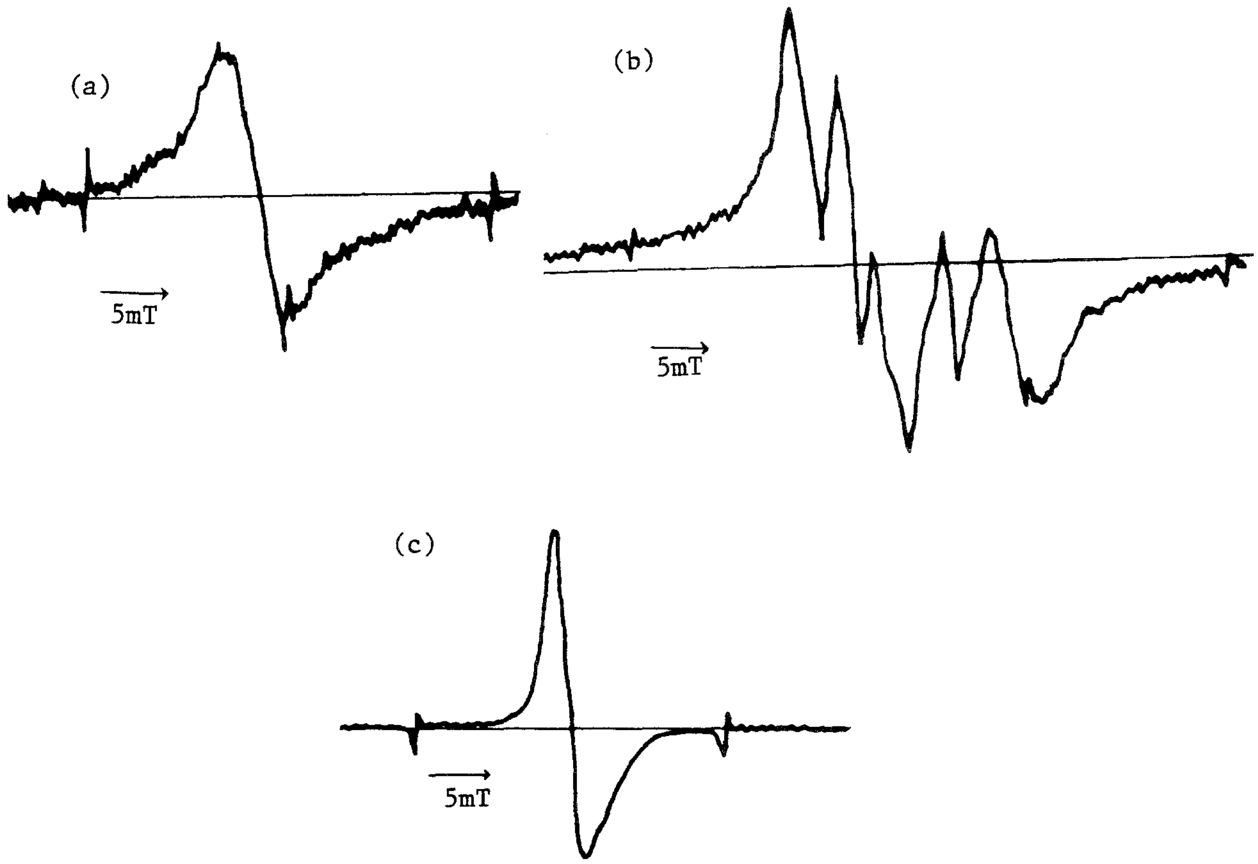

Figure 3 E.s.r. spectra of catalysts: (a) catalyst described in run 1 in *Table 1*; (b) catalyst described in run 6 in *Table 1*; (c) catalyst described in run 7 in *Table 1*. The conditions for measurement were described in Experimental section

Conclusions

The present results combined with the previous ones have led to the following conclusions.

(1) The effectiveness of the $TiCl_4.2THF$ catalyst combined with $AlCl_2(C_2H_5)$ and activated by TIBA can be markedly promoted when it is modified with an appropriate amount of $CoCl_2$ or $MgCl_2$.
(2) The use of an inappropriate amount of $MgCl_2$ or $CoCl_2$ causes the formation of different active catalyst species, resulting in heterogeneity of the catalyst system.
(3) The use of an excess amount of $MgCl_2$ or $CoCl_2$ causes over-reduction of the titanium species, resulting in a decrease in propene insertion into the polymer chain. These compounds are added into the catalyst synthesis as complexes with THF, which can poison the catalyst sites, thus this Lewis base must be removed from the catalyst. THF can be removed with Lewis acid, such as ethylaluminium dichloride; however, this kind of compound can cause the over-reduction of Ti at high concentration.
(4) The catalyst system gives poly(ethylene-*co*-propene), the structure of which is, in some cases, statistically random, depending on the Mt/Ti molar ratio.

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