Effects of the Type and Concentration of Alkylaluminum Cocatalysts on the Molar Mass of Polypropylene Made with *In Situ* Supported Metallocene Catalysts

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ABSTRACT: Propylene homopolymerizations were carried out with *rac*-dimethylsilylenebis(indenyl)zirconium dichloride, methylaluminoxane-modified silica, and common alkylaluminum cocatalysts. Supported catalysts were prepared by the *in situ* immobilization technique. The effects of the type and concentration (Al/Zr = 40–1000) of alkylaluminum on the propylene polymerization were evaluated with triethylaluminum (TEA), isoprenylaluminum (IPRA), and triisobutylaluminum (TIBA) as cocatalysts. The polymers were analyzed by gel permeation chromatography, differential scanning calorimetry, and ^{13}C-NMR. The polypropylene molar mass varied according to the nature of the alkylaluminum in the following order: TIBA > IPRA > TEA > no alkylaluminum. The polymers made with an *in situ* supported catalyst had lower crystallinities and melting points than the ones produced by homogeneous polymerization. The isotacticity was not affected by the polymerization conditions examined in this investigation. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1050–1055, 2005

Key words: catalysts; molecular weight distribution/molar mass distribution; poly(propylene) (PP)

INTRODUCTION

The advantages of using metallocene catalysts are well known and fully reported in the scientific literature.[1–4] These unique catalysts have the ability to produce polymers with narrow molar mass distributions and uniform comonomer incorporation. Therefore, polymers and copolymers produced by metallocenes can have significantly lower contents of low-molar-mass, waxlike fractions, providing excellent organoleptic properties. Besides, the molar masses, terminal groups, stereochemistry, and short-chain and long-chain branching can be controlled as functions of the metallocene structure.[5]

Although metallocene catalysts have higher activity under homogeneous polymerization conditions, they need to be heterogenized to be adapted to most existing polymerization processes.[6] There are four main methods of heterogeneization:[7]

1. Impregnation of the metallocene onto the support surface, which effectively means physisorption or chemisorption of the metallocene.
2. Adsorption of the metallocene/methylaluminoxane (MAO) adduct onto the support surface.
3. Initial impregnation of MAO onto the support followed by adsorption and simultaneous activation of the metallocene.
4. Covalent bonding of the metallocene by its ligand environment to the support, followed by activation of the metallocene with external MAO.

All these procedures have advantages and disadvantages and may lead to catalysts that produce polymers with different properties. Nevertheless, all the proposed routes are time-demanding, involving reaction and washing steps.[8] To overcome these problems, an alternative methodology (*in situ* immobilization) has been proposed and used to evaluate ethylene homopolymerization and copolymerization.[9–14] This approach consists of simultaneously adding the sup-

port [commercial methylaluminoxane-treated silica (SMAO)], the catalyst solution, and the cocatalyst (alkylaluminum) directly into the polymerization reactor, without the need of either external MAO or precontact among the species before polymerization. More recently, the *in situ* immobilization procedure has also been used in ethylene homopolymerization[15] and copolymerization[16] with a newly synthesized pentamethylene-bridged dinuclear zirconocene catalyst. Once again, the polymers had good morphology and replicated the morphology of the support.

In our previous publication, we showed that *rac*-dimethylsilylenebis(indenyl)zirconium dichloride [Me₂Si(Ind)₂ZrCl₂] prepared by *in situ* immobilization on SMAO polymerized propylene in the presence of common alkylaluminums such as triethylaluminum (TEA), isoprenylaluminum (IPRA), and triisobutylaluminum (TIBA). The polymers obtained with the *in situ* supported catalyst had lower values of the melting temperature (T_m), crystallization temperature, and crystallinity (χ) than those made with the homogeneous catalyst. On the other hand, polymers produced with the *in situ* supported systems had higher molar masses than those synthesized with the homogeneous catalyst at the same Al/Zr ratio. The tacticity did not vary with the catalytic system, and this showed that the stereoselectivity of the catalyst was not affected by the support. Scanning electron micrographs showed that the polymers obtained with *in situ* and conventionally supported systems had a well-defined morphology, unlike the polymers made with the homogeneous system, and this confirmed that there was no significant extraction of the catalyst from the silica support during the polymerization of propylene. Moreover, the concentration of the catalyst used was below the saturation level (2.0 wt % Zr/SMAO), and this indicated that all or almost all of the catalyst present in the solution was adsorbed onto the support.[17]

In this investigation, we evaluated the effect of the type and concentration of the alkylaluminum cocatalyst on propylene polymerization with *in situ* supported Me₂Si(Ind)₂ZrCl₂. The polymer products were characterized with differential scanning calorimetry (DSC) and gel permeation chromatography (GPC). To estimate the number of active site types present in the catalytic system and to evaluate the alkylaluminum effect on the polymer generated by each active center type, we deconvoluted GPC curves into Flory's most probable distributions.

EXPERIMENTAL

Materials

All the experiments were performed under an inert atmosphere with Schlenk techniques. The catalyst Me₂Si(Ind)₂ZrCl₂ (Witco, Bergkamen, Germany), MAO-modified silica (SMAO, 23 wt % Al; Witco, Bergkamen, Germany), and TEA, IPRA, and TIBA (all from Akzo,

Chicago, IL) were used without purification. Propylene was used as received from the cracker (Copesul, Triunfo, RS, Brazil), without any further purification. Toluene (Merck, Sâo Paulo, Brazil) and hexane were purified via refluxing over sodium and distillation. Hexane (Conoco Phillips, Borger, TX) was degassed with bubbling nitrogen before each reaction.

Polymerizations

The polymerizations were performed in a 1.5-L stainless reactor equipped with a mechanical stirrer, a constant-temperature circulator, and inlets for nitrogen and propylene. The reactor was filled with SMAO (Al/Zr = 500 mol/mol), 0.75 L of hexane, 10 mL of a catalyst solution (10^{-5} mol of the catalyst in toluene), and alkylaluminum. When the mixture reached 60°C, the stirring rate was set at 750 rpm, and the reactor was pressurized with propylene up to 6.0 bar (partial pressure) for 60 min. Acidified ethanol was used to quench the process. The polymer product was filtered, washed with distilled water, washed with ethanol, and dried at 80°C *in vacuo*. The mass of the dry polymer was measured to determine the product yield. Each polymerization reaction was repeated at least twice, and all the results presented in this article are the averages of these values.

Polymer characterization

χ and T_m were determined with a TA Instruments 2920 (New Castle, DE) differential scanning calorimeter according to ASTM D 3417/97 and ASTM D 3418/97. Two scans were performed, but only the results of the second scan were reported here. The heating rate was 10°C/min from 30 to 220°C, and the analysis was performed under a nitrogen atmosphere. The molar mass distribution was determined by high-temperature GPC with a Waters model 150C instrument (Milford, MA) equipped with four GMHXL-HT columns (TosoHaas, Tokyo, Japan) at 138°C. 1,2,4-Trichlorobenzene was used as the mobile phase. The columns were calibrated with 18 polystyrene and 3 polyethylene standards. The deconvolution of the polymer molar mass distribution was performed with an Excel spreadsheet.

The polymer microstructure was determined by ¹³C-NMR. The spectra were obtained at 135°C in a Varian Inova 300 (Palo Alto, CA) operating at 75 MHz. The polymer solutions were prepared in *o*-dichlorobenzene and benzene-d_6 (20% v/v) in 5-mm sample tubes. Spectra were taken with a 74° flip angle, an acquisition time of 1.5 s, and a delay of 4.0 s.

RESULTS AND DISCUSSION

The catalytic activities and average polypropylene properties are shown in Table I. For comparison,

TABLE I
Catalytic Activity of the $Me_2Si(Ind)_2ZrCl_2$/SMAO System in the Presence of TEA, TIBA, or IPRA and the Properties of the Polypropylenes Obtained with Homogeneous and *in situ* Polymerization

Alkylaluminum		Activity (kg of PP/g of catalyst h)	T_m (°C)	χ (%)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n
Type	Concentration (mol/mol)[a]						
Homogeneous polymerization[b]		4.6	142	53	16	34	2.1
	70	0.3	142	41	22	45	2.1
	250	0.4	141	27	20	42	2.1
TEA	500	0.3	140	25	16	30	1.9
	1000	0.1	140	18	14	26	1.8
	40	0.4	140	31	24	58	2.4
	70	0.5	139	42	24	53	2.2
TIBA	130	0.4	140	35	28	62	2.2
	250	0.6	141	33	30	63	2.1
	500	0.2	140	26	33	68	2.1
	1000	0.2	141	29	34	69	2.0
IPRA	130	0.8	141	44	22	47	2.2
	500	0.2	139	36	28	61	2.2

[a] $Al_{alkylaluminum}$/Zr ratio.
[b] Al_{MAO}/Zr = 500 mol/mol, without external alkylaluminum.

data from a homogeneous polymerization with MAO as the cocatalyst were included. As previously reported,[9,10] all reactions performed via *in situ* immobilization were less active than the homogeneous polymerization.

Alkylaluminum cocatalysts have been thought to act as scavengers, alkylating agents, and cocatalyst activators with *in situ* supported metallocenes.[9] The activity of $Me_2Si(Ind)_2ZrCl_2$/SMAO was practically independent of the type of alkylaluminum used in the polymerization (Table I), but the catalyst system had maximum activity with IPRA at an Al/Zr ratio of 130. For all systems (TEA, TIBA, and IPRA), the activity decreased as the cocatalyst concentration increased.

According to the DSC results, the polymers obtained via *in situ* immobilization of the catalyst in the presence of an alkylaluminum showed lower T_m and χ values than the polymer produced in the homogeneous polymerization. It seems that the heterogeneous nature of the surface species generated in the case of the *in situ* supported $Me_2Si(Ind)_2ZrCl_2$ might have led to a reduction in χ of the resulting polypropylene.

The tacticity of some samples, including the polymer obtained in the homogeneous polymerization, was calculated with ^{13}C-NMR. All of them were highly isotactic (m = 92.7–94.0%), and this indicated that the stereoregularity was influenced neither by the type of the cocatalyst nor by the immobilization procedure.

Except for the polymers produced with Al/Zr ≥ 500 mol/mol with TEA, all the others had higher molar masses than that of polypropylene produced with the homogeneous catalyst. This behavior is typical of supported zirconocenes and has been attributed to the blocking of the polymerization active sites by the support, which probably reduces β-elimination transfer reactions.[18]

The molar mass was influenced by the concentration and type of alkylaluminum. The molar mass decreased with increasing amounts of TEA. On the other hand, it increased with increasing amounts of TIBA or IPRA. This result clearly indicated that chain transfer to alkylaluminum was more relevant with TEA than with TIBA and IPRA, probably because of the intrinsic steric effects played by the two latter alkylaluminum cocatalysts.

For the same concentration of alkylaluminum, the polymer molar mass decreased in the following order: TIBA > IPRA > TEA. Similar results were obtained for polyethylenes produced with *in situ* supported rac-ethylenebis(indenyl)zirconium dichloride ($Et(Ind)_2ZrCl_2$.)[14] Alkylaluminums with bulkier ligands, such as TIBA and IPRA, may reduce the occurrence of terminations by chain transfer to cocatalyst, leading to polymers with higher molar masses.[19] These results support the idea that the alkylaluminum not only acts as a scavenger but also has some influence on the formation of active centers.

The influence of alkylaluminums used as cocatalysts on the molar mass of polypropylene has already been reported in the literature for homogeneous and heterogeneous polymerizations. For propylene homopolymerizations and 1-hexene copolymerizations with $Et(Ind)_2ZrCl_2$ with TIBA/MAO mixtures, the molar mass of the polymers increased with the addition of TIBA, without any change in the isotacticity or in the concentration of the comonomer incorporated.[20] The molar mass of the polypropylene prepared with $Et(Ind)_2ZrCl_2$ or $Me_2Si(Ind)_2ZrCl_2$ in the presence of $TEA/Ph_3CB(C_6F_5)_4$ decreased when the amount of TEA increased. However, when $TIBA/Ph_3CB(C_6F_5)_4$ was used as cocatalyst, the molar mass did not change. Moreover, comparing the polymers obtained with

TABLE II
GPC Deconvolution Curves of M_n and the Fraction of the Polymer Generated by Each Active
Center Type with TEA, TIBA, or IPRA as the Cocatalyst

Alkylaluminum		Peak/active center I		Peak/active center II		Peak/active center III	
Type	Concentration (mol/mol)[a]	M_n (kg/mol)	Fraction (%)	M_n (kg/mol)	Fraction (%)	M_n (kg/mol)	Fraction (%)
Homogeneous polymerization[b]		8.1	23	19	77	—	—
TEA	70	8.6	16	23	78	57	6
	250	7.4	18	21	69	41	13
	500	9.7	44	20	56	—	—
	1000	9.7	74	22	26	—	—
TIBA	40	10	22	26	57	54	21
	70	9.6	19	23	52	42	29
	130	7.7	7	21	37	40	56
	250	5.7	4	18	29	38	67
	500	9.8	11	32	63	47	26
	1000	11	8	33	84	70	8
IPRA	130	11	26	23	63	59	11
	500	9.8	16	30	76	79	8

[a] $Al_{alkylaluminum}/Zr$ ratio.
[b] Al_{MAO}/Zr = 500 mol/mol, without external alkylaluminum.

both catalysts, we found that the ones prepared in the presence of TIBA/Ph$_3$CB(C$_6$F$_5$)$_4$ had a molar mass higher than or equal to that of polymers prepared with TEA/Ph$_3$CB(C$_6$F$_5$)$_4$.[21] Polypropylenes obtained with the heterogeneous system rac-ethylenebis(tetrahydroindenyl)zirconium dichloride (Et(IndH$_4$)$_2$ZrCl$_2$)/MAO/SiO$_2$ in the presence of TMA, TEA, or TIBA had higher molar masses than those synthesized in the absence of alkylaluminum. The molar mass of the polymers decreased according to the following order: TIBA > TEA ≥ TMA.[22]

The polydispersity index of the polymers made in the presence of TEA or TIBA decreased when the concentration of the alkylaluminum increased. With IPRA, this effect was not observed, but it should be taken into account that only two Al/Zr ratios were examined with this cocatalyst.

To estimate the number of active centers present in the catalytic system and to evaluate the alkylalumi-

num effect on the polymer generated by each active center type, we deconvoluted the GPC curves into Flory's most probable distributions.[23,24] The results are shown in Table II. Catalyst–surface interactions might have led to the formation of sites of different types. Although the GPC curves of polymers produced with the homogeneous (unsupported) catalyst were deconvoluted into two peaks (indicating the presence of two active center types), the GPC curves of almost all the polymers prepared via *in situ* immobilization required three peaks. The only exceptions were the polymers produced with Al/Zr ratios of 500 and 1000 mol/mol of TEA, for which the best fit was obtained with only two peaks. Figures 1 and 2 show examples of GPC curves and their respective deconvolutions into Flory's most probable distributions.

The polymer molar mass assigned to each active center type decreased with increasing Al/Zr ratio until a value of 250 mol/mol was reached. When this
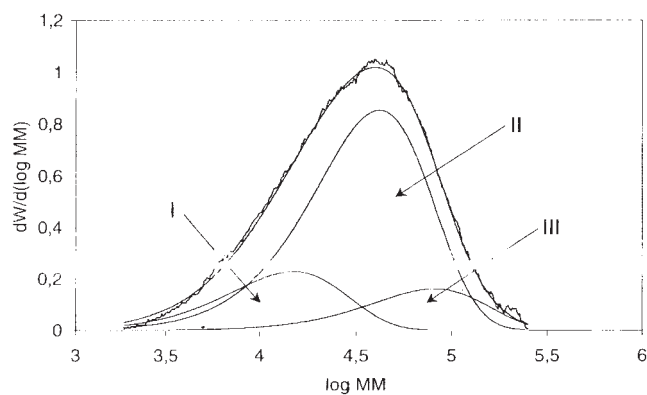

Figure 1 Molar mass distribution deconvolution of the polymer prepared with 250 mol/mol of TEA as a cocatalyst.
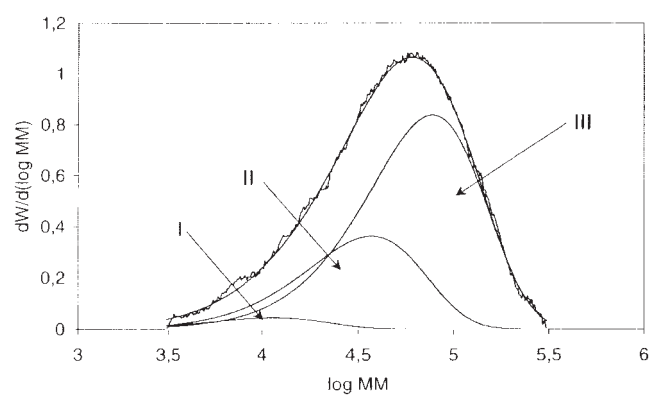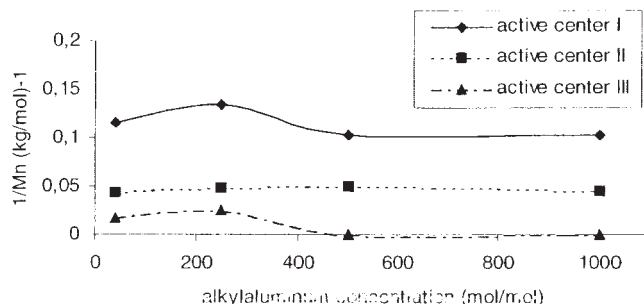

Figure 2 Molar mass distribution deconvolution of the polymer prepared with 250 mol/mol of TIBA as a cocatalyst.

Figure 3 Effect of the TEA concentration on $1/M_n$ of the polymer formed by each active center type.

Figure 4 Effect of the TIBA concentration on $1/M_n$ of the polymer formed by each active center type.

ratio was further increased, the molar mass per active site type started increasing (Table II).

Comparing the polymerizations carried out with TEA or TIBA at the same concentration of alkylaluminum, we found that the amount of polymer generated by active center I with TEA was higher than that with TIBA. On the other hand, the amount of polymer formed by active center III was higher when TIBA was used. This suggested that TEA might have caused a selective deactivation of active center III that was responsible for the highest molar mass population.

The reciprocal of the number-average molar mass $(1/M_n)$ of the polymer chains made on each active center may be related to the τ parameter, the ratio of the chain transfer rates to the chain propagation rate:[25–27]
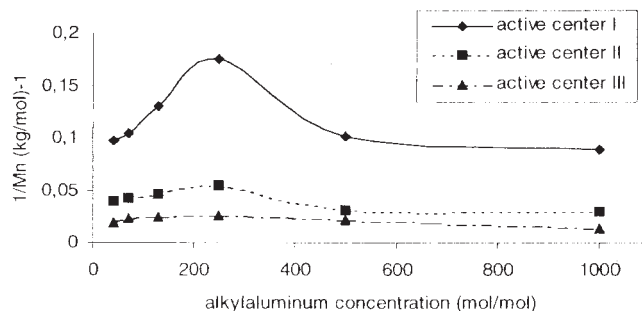
$$\frac{1}{M_n} = \tau = \frac{k_m}{k_p} + \frac{k_\beta}{k_p [M]} + \frac{k_{Al} [Al]}{k_p [M]} + \frac{k_{H_2} [H_2]}{k_p [M]} \quad (1)$$

where k_m is the rate constant of chain transfer to the monomer, k_β is the β-hydride elimination rate constant, k_{Al} is the rate constant of chain transfer to alkylaluminum, k_{H_2} is the rate constant of chain transfer to hydrogen, k_p is the chain propagation rate constant, $[M]$ is the monomer concentration, $[Al]$ is the alkylaluminum concentration, and $[H_2]$ is the hydrogen concentration.

As in all polymerizations carried out in this investigation, the monomer concentration was kept constant, and hydrogen was not used, we could assume that eq. (1) could be simplified to

$$\frac{1}{M_n} = k' + \frac{k_{Al} [Al]}{k_p [M]} = k' + k'' [Al] \quad (2)$$

This simplification assumed that k_p was independent of the alkylaluminum concentration. This assumption could not be proved with the data presented in this work and could, at least partially, explain the deviations observed between the mathematical model and the experimental data discussed later.

Figures 3 and 4 show the effects of the concentration of TEA or TIBA on the reciprocal of M_n for polymers made by each active center type; they are based on the molar mass deconvolution results.

The same behavior was observed for both alkylaluminums: up to approximately Al/Zr = 250 mol/mol, $1/M_n$ increased as the TEA or TIBA concentration increased, according to the predictions of eq. (2). However, for higher amounts of alkylaluminum, $1/M_n$ decreased with increasing Al/Zr ratios. These results indicated that eq. (2) was valid only when low concentrations of the alkylaluminum were used (0–250 mol/mol), not being valid for higher concentrations.

A simple empirical correlation could be derived for the dependence of M_n on the Al/Zr ratio when the molar mass of the whole polymer was considered (Table III).

Figure 5 shows that there was a linear relationship between $1/M_n$ of the total polymer and the TEA concentration:

$$\frac{1}{M_n} = k_1 + k_2 [TEA] \quad (3)$$

On the other hand, $1/M_n$ was proportional to the reciprocal of the square root of the TIBA concentration, as shown in Figure 6 and quantified here:

TABLE III
Effect of the Alkylaluminum Concentration on the Reciprocal of M_n of the Total Polymer Prepared with TEA or TIBA as the Cocatalyst

Type	Alkylaluminum Concentration (mol/mol)[a]	$1/M_n$ (kg/mol)$^{-1}$
TEA	70	0.045
	250	0.050
	500	0.063
	1000	0.071
TIBA	40	0.042
	70	0.042
	130	0.036
	250	0.033
	500	0.030
	1000	0.029

[a] $Al_{alkylaluminum}/Zr$ ratio.

$$\frac{1}{M_n} = k_3 + \frac{k_4}{\sqrt{[\text{TIBA}]}} \tag{4}$$

CONCLUSIONS

Polypropylene prepared with *in situ* supported $Me_2Si(Ind)_2ZrCl_2$ through the direct contact of the catalyst with SMAO in the presence of TEA, TIBA, or IPRA had, in comparison with the polymer obtained with a homogeneous catalyst at an Al_{MAO}/Zr ratio of 500, lower χ and T_m values, similar isotacticities and polydispersity indices, and higher molar masses.

The catalytic activity decreased when the alkylaluminum concentration increased, almost independently of the cocatalyst type. Catalysts with IPRA had slightly higher activities for all the systems studied.

The polymer molar mass was influenced by the type and concentration of the alkylaluminum. When the concentration of TEA increased, the molar mass decreased. On the other hand, with TIBA and IPRA, the molar mass increased as the alkylaluminum concentration increased. For the same alkylaluminum concentration, the polymer prepared with TIBA had the highest molar mass, whereas the one obtained with TEA had the lowest.

Although the difference in the values could be considered small, the polydispersity decreased with increasing amounts of TEA or TIBA. The polydispersity did not change with various amounts of IPRA in the limited range of this investigation.

According to the GPC curve deconvolution, the *in situ* supported catalysts seemed to present a larger number of distinct active centers than the homogeneous one, and this suggested that the catalyst was in fact heterogenized onto the support surface.

The molar mass of the polymer made on each active center type decreased as the Al/Zr ratio increased up to 250 mol/mol. Up to this concentration, there was a linear relationship between the reciprocal of M_n and the alkylaluminum concentration. When the cocatalyst concentration was further increased, this relationship was no longer observed.
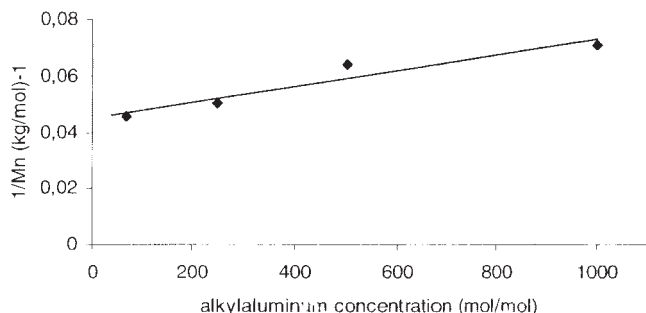
Figure 5 Effect of the TEA concentration on $1/M_n$ of the total polymer.
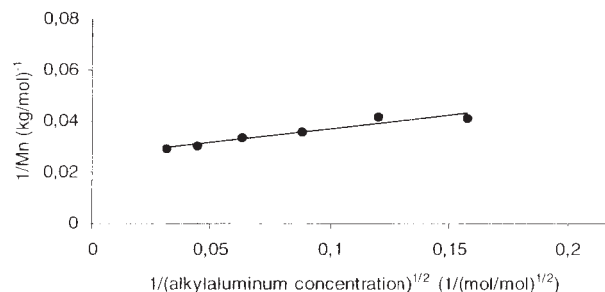
Figure 6 Effect of the TIBA concentration on $1/M_n$ of the total polymer.

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