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Polymerization of Conjugated Dienes Promoted by Bis(phenoxyimino)titanium Catalysts

J. Antonio Lopez-Sanchez, Marina Lamberti, Daniela Pappalardo, and Claudio Pellecchia*

Dipartimento di Chimica, Università di Salerno, I-84081 Baronissi (SA), Italy

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Introduction

The design of new "non-metallocene" catalysts for olefin polymerization has been an increasingly appealing target for academic and industrial researchers over the past 5 years.[1] In particular, an interesting new class of catalysts based on bis(phenoxyimino) group 4 metal derivatives has been developed by Fujita and co-workers.[2] Certain Zr complexes of this class afford some of the most active ethylene polymerization catalysts, while some Ti complexes are able to promote the syndiotactic-specific polymerization of propene and the living polymerization of olefins above room temperature.[2]

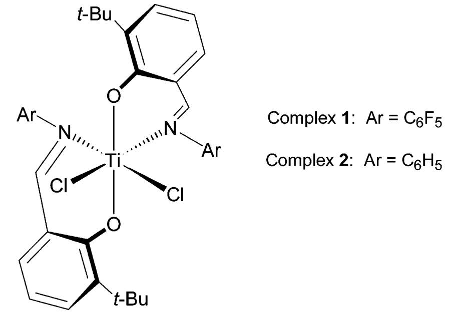
Although a number of papers have reported the activity of these catalytic systems in the homo- and copolymerization of various monomers, no data are available in the literature concerning the homopolymerization of 1,3-alkadienes. In this paper we report our results obtained in the homopolymerization of 1,3-alkadienes promoted by two prototypical bis(phenoxyimino)-Ti(IV) complexes and a comparison with the well-known half-metallocene catalyst based on $CpTiCl_3$.[3]

Experimental Section

Materials. Manipulations of sensitive materials were carried out under a dry nitrogen atmosphere using Schlenk or glovebox techniques. Toluene was refluxed over metallic sodium and distilled under a nitrogen atmosphere before use. Methylaluminoxane (MAO, Aldrich) was purchased as a 10 wt % solution in toluene and used as received. The bis(phenoxyimino)Ti(IV) complexes **1** and **2** were synthesized as reported in the literature.[4] $CpTiCl_3$ (97%) was commercially obtained from Aldrich and used straightforwardly. 1,3-Butadiene (99.5%) was purchased from Società Ossigeno Napoli (SON) and used without further purification. Isoprene (99%), (*Z*)-1,3-pentadiene (98%), and (*E*)-1,3-pentadiene (96%) were purchased from Aldrich. 4-Methyl-1,3-pentadiene (98%) was purchased from Fluka AG. All these monomers were purified by trap-to-trap distillation in the presence of $Al(C_2H_5)_3$.

Polymerizations. The polymerization conditions are detailed in the corresponding polymerization results tables. In a typical run, temperature was maintained constant by using a thermal bath. The monomer was injected as a liquid into a round flask (50 mL) containing toluene and the desired cocatalyst and stirred at the selected temperature; immediately afterward, a toluene solution (5 mL) containing the precatalyst complex was added. After the selected polymerization time, the polymers were coagulated in an excess of acidified ethanol, washed several times, and dried in vacuo at room temperature. As an example, run 1 was carried out injecting, under a nitrogen atmosphere, 0.5 g of butadiene (9.250 mmol) in a stirred 50 mL glass round flask containing 3.9 mL of a MAO solution in toluene (6.250 mmol) and 10 mL of dry toluene. The reactant mixture was thermostated at 20 °C in a thermal bath. The polymerization was initiated by adding a solution of 0.010 g of precatalyst **1** (0.0125 mmol) in 5 mL of toluene. After 60 min, the polymerization mixture was precipitated in a 500 mL Erlenmeyer flask containing ca. 200 mL of ethanol acidified with a small amount of HCl. The precipitated polymer was filtered and washed with ethanol several times. The polybutadiene obtained was then dried in vacuo at room temperature for ca. 8 h and weighted (0.39 g, 78% conversion). The relative amount of 1,2-units (8%) in the microstructure of the polymer was evaluated using ^1H NMR, whereas the relative amount of 1,4-cis (84%) and 1,4-trans (8%) units was evaluated by ^{13}C NMR. GPC analysis of the polymer resulted in the following parameters: $\bar{M}_w = 6.12 \times 10^5$ g mol^{-1}, $\bar{M}_n = 1.26 \times 10^5$ g mol^{-1}, and $\bar{M}_w/\bar{M}_n = 4.9$ g mol^{-1}.

Scheme 1. Bis(phenoxyimino)titanium Precatalysts Utilized in Polymerization Tests of 1,3-Alkadienes



Analysis of the Polymers. The polymers were analyzed by NMR on a 300 MHz Bruker spectrometer operating in the Fourier transform mode. The spectra were recorded in $CDCl_3$ at ambient temperature and referenced vs TMS. The structure of the polymers was assigned by comparing the chemical shifts of the resonances observed in the spectra and the data reported in the literature for *cis*-1,4-polybutadiene,[5] *cis*-1,4-polyisoprene,[6] 1,4-poly(1,3-pentadienes),[3a,7] and syndiotactic 1,2-poly-(4-methyl-1,3-pentadiene).[8] The molecular weight distributions of the polymers were analyzed with a PSS SDV gel permeation chromatograph (GPC) containing three polystyrene divinylbenzene gel columns (100, 10^4, and 10^6 Å pore size), a WGE refraction index detector using $CHCl_3$ as eluent at 25 °C, a flow rate of 1 mL/min, and standard polystyrene samples for calibration.

Results and Discussion

The bis(phenoxyimino)Ti(IV) complexes used in this study are displayed in Scheme 1.

Complexes **1** and **2** were previously shown to promote, after activation with methylaluminoxane (MAO), the polymerization of ethylene[4] and propene,[9,10] in the latter case affording a syndiotactic polymer via a chain-end mechanism of steric control and 2,1 monomer insertion.[11] The catalyst derived from **1** resulted more active and more stereospecific than the catalyst based on **2**; moreover, the former catalyst was shown to afford the living polymerization of both ethylene and propene above room temperature.[10,12]

We tested both catalytic systems in the polymerization of butadiene at different temperatures. The main polymerization results and conditions are summarized in Table 1.

For comparison, run 14 was carried out in the presence of $CpTiCl_3$ (cyclopentadienyltitanium trichloride) and MAO under the same conditions used for **1** and **2** in runs 1 and 6, respectively. It produced lower yields

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* Corresponding author: Fax 39 089 965296; e-mail cpellecchia@unisa.it.

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Table 1. Butadiene Polymerization Results[a]

run	precatalysts	cocatalyst	temp (°C)	polym time (h)	yield (g)	conv (%)	polymer microstructure cis-1,4 (%)	trans-1,4 (%)	1,2 (%)
1	**1**	MAO	20	1	0.39	78	84	8	8
2[b]	**1**	MAO	20	1	1.24	62	86	5	9
3	**1**	MAO	0	24	0.20	40	85	7	8
4	**1**	MAO	−20	24	0.09	18	75	15	10
5[b]	**1**	MAO	−20	24	0.10	5	83	7	10
6	**2**	MAO	20	1	0.5	99	83	9	8
7[b]	**2**	MAO	20	1	1.99	99	85	6	9
8	**2**	MAO	0	24	0.23	46	83	7	10
9	**2**	MAO	−20	24	0.16	32	78	10	12
10[b]	**2**	MAO	−20	24	0.34	17	79	7	14
11	**2**	MAO	−30	24	0.06	11	79	8	13
12	**2**	MAO	−50	24	*g*	<1			
13	**2**	MAO[c]	20	1	0.10	20	79	10	11
14	CpTiCl$_3$	MAO	20	1	0.30	60	82	10	8
15	**2**	AlMe$_3$[d]	20	1	0	0			
16	**2**	AlEt$_3$[e]	20	1	0	0			
17	**2**	[Ph$_3$C][B(C$_6$F$_5$)$_4$]/Al(*i*-Bu)$_3$[f]	20	1	0	0			

[a] Polymerization conditions: 0.5 g of monomer, 10 mL of toluene, cocatalyst: Al/Ti = 500, 12.5 μmol of complex. [b] 2 g of monomer and 50 mL of toluene were used. [c] Solid MAO obtained by distilling off the solvent under reduced pressure at 60 °C. [d] 2.5 mmol of AlMe$_3$. [e] 0.38 mmol AlEt$_3$. [f] Combination of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (25 μmol) and triisobutylaluminum (0.625 mmol). [g] Traces.

of polybutadiene (0.30 g, 60% conversion) when compared to the bis(phenoxyimino) catalytic systems.

The microstructures of the polybutadienes were analyzed by ^{1}H and ^{13}C NMR spectroscopy. The relative amounts of *cis*-1,4, *trans*-1,4, and 1,2 insertions are displayed in Table 1. The structure of the polymers obtained with complexes **1** and **2** at 20 °C is prevailingly *cis*-1,4 in both cases with minor amounts of *trans*-1,4 and 1,2 units. A similar microstructure was observed for the polymer obtained in the presence of CpTiCl$_3$/MAO. By decreasing temperature to subzero values, the activity of the catalyst drastically decreases while the structure of the polymer is only slightly affected, by means of an increase in the relative amount of 1,2 insertions (see runs 7−11).

According to these results, the catalytic systems based on complexes **1** and **2** are more active than those based on CpTiCl$_3$. The highest activity observed was of 159 kg of polymer (mol of Ti)$^{-1}$ h^{-1}, corresponding to complex **2** in run 7. Miyatake et al.[13] reported butadiene polymerization results obtained with 2,2′-thiobis(6-*tert*-butyl-4-methylphenoxy)titanium diisopropoxide and MAO at 60 °C. Similarly, they obtained a polybutadiene prevailingly *cis*-1,4(>96%) and reported an activity of 53 kg of polymer (mol of Ti) $^{-1}$ h $^{-1}$.

The perfluorinated complex **1** affords a slightly less active catalyst than complex **2**, in contrast to what was observed in propylene and ethylene polymerization, where a significant enhancement in the catalyst activity was achieved by introducing a perfluorinated aniline substituent. The latter effect was ascribed to the generation of a more electropositive metal center due to the electron withdrawing of the fluorine substituents.[2] In the case of butadiene, the different trend could be due to the higher nucleophilicity of this monomer with respect to a simple olefin.

Some additional runs were carried out to investigate the possible effect of the cocatalyst in these systems. Thus, run 13 was performed by using complex **2** and solid methylaluminoxane (obtained by distilling off the solvent from the commercial MAO solution). A significantly lower conversion was observed (20% vs 60%), while the polybutadiene microstructure was substantially identical. AlMe$_3$ (2.5 mmol) and AlEt$_3$ (0.38 mmol) were also used as cocatalysts instead of MAO, resulting in complete loss of polymerization activity (runs 15 and 16). Finally, a combination of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (25 μmol) and triisobutylaluminum (0.625 mmol) was used as cocatalyst, also resulting in no catalytic activity (run 17). For related Zr-based catalytic systems, Fujita et al.[12] suggested that the imine function is reduced in the presence of [Ph$_3$C][B(C$_6$F$_5$)$_4$] and triisobutylaluminum, resulting in the in situ generation of a phenoxy−amine complex: it is thus possible that the latter is not active for butadiene polymerization.

Table 2. Isoprene Polymerization Results[a]

run	precatalyst	temp (°C)	yield (g)	conv (%)
18	**1**	20	0.07	3.5
19	**2**	20	0.05	2.5
20	**2**	50	0.64	32
21	**2**	70	0.15	7
22	CpTiCl$_3$	20	*b*	<1
23	CpTiCl$_3$	50	*b*	<1

[a] Polymerization conditions: 2 g of monomer, 10 mL of toluene, cocatalyst: MAO (Al/Ti = 500), 12.5 μmol of complex, and 4 h polymerization time. [b] Traces.

Polymerization tests were also performed with other dienes. The results of some isoprene polymerizations with catalysts based on **1** and **2** and, for comparison, with CpTiCl$_3$−MAO are reported in Table 2.

At 20 °C the conversion is rather low for both **1** and **2**, although it is higher than that obtained with CpTiCl$_3$−MAO. At this polymerization temperature the microstructure of the polymer obtained is predominantly *cis*-1,4 (94%), and only a minor amount of 3,4 insertions is detected (6%). Increasing the reaction temperature to 50 °C results in a significant enhancement in the polymerization rate for complex **2**−MAO (see run 20), while CpTiCl$_3$−MAO under the same conditions remains substantially inactive (see run 23). The increase of the polymerization temperature has also an effect on the chemoselectivity of the catalyst: indeed, polymers produced at 50 and 70 °C suffer an increase of the relative amount of 3,4 insertions (15%) and a decrease of 1,4-cis insertions (85%).

The molecular weights for some selected polymers were measured by GPC in chloroform at 25 °C (see Table 3).

Bis(penoxyimino)titanium catalysts afford polybutadienes having significantly higher molecular weights

Table 3. Molecular Weights of Selected Polybutadiene and Polyisoprene Samples, Obtained by GPC in $CHCl_3$ at 25 °C

run	catalyst complex	monomer	polym time (h)	$\bar{M}_w \times 10^5$	$\bar{M}_n \times 10^5$	$\bar{M}_w/\bar{M}_n$
1	**1**/MAO	1,3-butadiene	1	6.12	1.26	4.9
6	**2**/MAO	1,3-butadiene	1	4.03	1.39	2.9
14	$CpTiCl_3$/MAO	1,3-butadiene	1	1.34	0.34	4.0
18	**1**/MAO	isoprene	4	6.20	1.75	3.6

Table 4. Pentadiene Polymerization Results[a]

run	monomer	precatalysts	temp (°C)	polym time (h)	yield (g)	conv (%)	microstructure 1,4-cis (%)	microstructure 1,4-trans (%)	microstructure 1,2 (%)
24	(*Z*)-1,3-pentadiene	**1**	20	4	0.22	11	99		
25	(*Z*)-1,3-pentadiene[b]	**2**	20	4	0.05	4.5	99		
26	(*Z*)-1,3-pentadiene[b]	**2**	−20	4	*c*	<1			
27	(*Z*)-1,3-pentadiene[b]	**1**	0	24	0.14	14	99		
28	(*Z*)-1,3-pentadiene[b]	**1**	−20	24	0.01	<1	99		
29	(*E*)-1,3-pentadiene	**1**	20	4	1.25	63	34	66	
30	(*E*)-1,3-pentadiene	**2**	20	4	1.26	63	57	43	
31	(*E*)-1,3-pentadiene	**2**	−20	4	0.37	19	51	49	
32	4-methyl-1,3-pentadiene	**1**	20	4	0.20	10		14	86

[a] Polymerization conditions: 2 g of monomer, 10 mL of toluene, cocatalyst: MAO (Al/Ti = 500), 12.5 μmol of complex. [b] 1 g of monomer was used. [c] Traces.

than those produced by $CpTiCl_3$ under identical conditions. The molecular weight distributions are in all cases broader than expected for single-site catalysts. Recent results reported in the literature point to the possibility of equilibria between different isomeric active complexes for bis(phenoxyimino) catalysts.[14]

Polymerization results for (*Z*)-1,3 pentadiene, (*E*)-pentadiene, and 4-methyl-1,3-pentadiene are summarized in Table 4.

The activity of catalyst **1**−MAO in the polymerization of (*E*)-1,3 pentadiene at 20 °C is 6 times higher than that observed for (*Z*)-1,3 pentadiene or 4-methyl-1,3-pentadiene, which are roughly the same. In the polymerization of (*Z*)-1,3 pentadiene the yields obtained with complexes **1** and **2** at 20 °C are comparable to those previously reported in the literature using $CpTiCl_3$/MAO.[3] Also, the polymer structure consists almost exclusively of *cis*-1,4 units. In the case of $CpTiCl_3$/MAO, Porri et al.[7] found an unusual temperature-dependent behavior in the polymerization of (*Z*)-1,3-pentadiene, which gives a prevailingly *cis*-1,4 polymer at 20 °C and a 1,2-syndiotactic polymer at −28 °C. Thus, two polymerization runs were carried out at 0 and −20 °C with catalyst **1**−MAO to investigate the presence of any related effect. The polymerizations were allowed to proceed for 24 h in order to obtain enough polymers for NMR analysis, since the activity was significantly reduced (see runs 26−28). The polymer structure, however, resulted in any case almost exclusively *cis*-1,4.

Conclusions

The bis(phenoxyimino)Ti(IV) complexes studied as precatalysts for the homopolymerization of conjugated dienes showed significant activities, comparable to or higher than those obtained with $CpTiCl_3$ under similar conditions. The activity of the catalyst varied depending on the monomer, with 1,3-butadiene affording the best results and (*E*)-1,3-pentadiene being significantly more reactive than (*Z*)-1,3-pentadiene and 4-methyl-1,3-pentadiene, similar to what was previously observed for $CpTiCl_3$. At 20 °C isoprene seems to be the less reactive of the 1,3-alkadienes tested, although a reasonable monomer conversion is achieved by increasing the temperature to 50 °C. This is not the case when $CpTiCl_3$−MAO is used, which is substantially inactive toward isoprene at any temperature. A significant decrease of catalysts activity is observed by decreasing the temperature of polymerization to subambient values. The microstructure of the polymers is in general very similar to that produced by the $CpTiCl_3$-based catalyst. For the latter catalyst, a recent theoretical study[15] rationalized the chemoselectivity of diene polymerization by assuming an active site containing one ancillary Cp ligand, besides the allyl-type growing chain and the coordinated monomer. In this framework, the similar chemoselectivities obtained with the bis(phenoximine) catalysts could imply a partial removal of the ancillary ligands of the precatalysts.

These results address a further peculiar feature of this class of catalysts with respect to metallocenes, i.e., their high activity vs both olefins and conjugated dienes. We are currently extending our investigation to the copolymerization of olefins and dienes as well as to mono(phenoxyimine)titanium catalysts.

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