Metal Supported Catalysts for PLA

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ABSTRACT

Ti(O^{i}Pr)$_4$/SBA-15 and TiCl(O^{i}Pr)$_3$/SBA-15 were prepared by immobilizing titanium(IV) tetraisopropoxido and titanium(IV) chlorido triisopropoxido, respectively, over pretreated mesoporous silica. A series of solution polymerizations of L-lactide were conducted with titanium alkoxidos as homogeneous catalysts and silica-supported titanium alkoxido catalysts to compare their catalytic activity and the characteristics of the polylactide (PLA) produced. Both homogeneous and supported systems achieved the same monomer conversion (higher than 90%), being the homogeneous catalyst faster. The PLA produced using Ti(O^{i}Pr)$_4$/SBA-15 presented higher molecular weights and T$_m$ than polymers obtained using TiCl(O^{i}Pr)$_3$/SBA-15.

V(O^{i}Pr)[ONNO], VO(O^{i}Pr)$_3$ and V(NAda)(O^{i}Pr)$_3$ were used in ring-opening polymerization of lactide in solution and bulk conditions. VO(O^{i}Pr)$_3$ revealed the most active catalyst and a good polymerization control was observed.

Keywords: Polylactide, Ring-opening polymerization, Mesopourous silica support, Titanium alkoxido catalyst, Vanadium complexes catalysts.

1. Introduction

Plastics play an extremely important role in modern society. However, most plastics are primarily based on petrochemical and non-renewable resources, which cause severe environmental and sustainability problems, resulting in special attention to use biodegradable polymers [1]. Polylactide (PLA) is an aliphatic polyester that is produced from lactic acid derived from renewable resources such as sugar beets or corn [2]. PLA is commonly synthesized by ring-opening polymerization (ROP) of lactide, which is a dimer of lactic acid. This synthesis route allow to produce PLA with high molecular weight and polymerization control [3]. PLA has excellent mechanical properties, becoming a good material for medical devices and industrial packaging materials [4]. Homogeneous metal catalysts, such as tin, aluminium, zinc alkoxidos, have been reported as the most common metal-containing species for ROP of lactide [5]. However, the heterogeneous catalyst systems are thought to be desirable in controlling the polymerization process and the easier separation of the catalyst from the polymer product. In this work, the characteristics of heterogeneous titanium alkoxido catalysts (Ti(O^{i}Pr)$_4$ and TiCl(O^{i}Pr)$_3$) using SBA-15 as a support are reported. A series of polymerizations in toluene solution of L-lactide were performed with both homogeneous and heterogeneous catalysts to compare the characteristics of the two catalyst systems.

Preliminary and innovative studies using vanadium complexes, (VO(O^{i}Pr)[ONNO], VO(O^{i}Pr)$_3$ and V(NAda)(O^{i}Pr)$_3$), as catalysts for ROP of lactide are also described.

2. Experimental

2.1. Material

L-lactide (Sigma-Aldrich) and *rac*-lactide were recrystallized from toluene and sublimed prior to

use. Toluene was pre-dried using 4 Å molecular sieves and refluxed under an atmosphere of N_2, and collected by distillation. Mesoporous silica (SBA-15), prepared as previously published [6], was used as support to immobilize the catalysts. Titanium tetraisopropoxido (Sigma, 97%) was used in toluene solution (0,05M). Titanium chloride triisopropoxido (Alfa Aesar 95%) was used as received. Vanadium complexes were synthesized by Coordination Chemistry Laboratory in University of Toulouse and placed under Argon in sealed ampules. All manipulations were performed under a dry nitrogen atmosphere.

2.2. Characterization

Specific surface measurements were performed using BET method (Micromeritics, ASAP 2010) at -196ºC using nitrogen as adsorption gas. Before the measurement, the sample was degassed at 300 ºC for 3 h. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to observe the morphologies of the support. The thermal analysis of the samples was performed by a thermogravimetric analyzer (TGA, TGA 92 SETARAM). The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI, defined as M_w/M_n) of the produced PLA were determined by gel permeation chromatography (GPC; for tests using titanium as catalysts: HPLC Waters chromatograph; for experiments using vanadium as catalysts: Shimadzu LC20AD ultra-fast liquid chromatography) using THF as solvent. The melting temperature (T_m) of the produced PLA was determined using differential scanning calorimetry (DSC, TA Instruments, DSC2980), using the second heating thermogram at a heating rate of 10ºC/min.

2.3. Preparation of Ti supported catalysts

SBA-15 was dried at a heating rate 5°C/min until 400°C under an air stream of 80 ml/min, kept at 400°C for 2 hours in air and 1 hour under nitrogen. Predetermined amounts of SBA-15 and titanium compound were suspended in 10 mL of dried toluene and the reactions were carried out in different conditions of time (1.5 hours and 3 hours) and temperature (50ºC and room temperature, *ca.* 21°C). Different amounts of titanium were immobilized to obtain different Ti(mmol)/SBA-15(g) ratios. After impregnation, the catalysts were used right away in the polymerization reactions.

2.4. Lactide polymerization with Ti supported catalysts

Solution polymerization of L-lactide was carried out using a schlenk tube equipped with a magnetic stirrer. Predetermined amounts of purified l-lactide, supported catalyst suspension in toluene or predetermined amounts of purified l-lactide, dried toluene and homogeneous catalyst were charged into a schlenk tube under nitrogen. The reactions were carried out under different conditions of temperature, time and L-lactide/Ti molar ratio. The reations were terminated by addition of 2 ml of water and the polymers were precipitated in an excess of methanol. The suspension was filtered under vacuum and the composite obtained was dried at 40°C under vacuum overnight.

2.5. Lactide polymerization with V supported catalysts

In bulk conditions, the desired initiator (1 eq., 5 mg) and *rac*-lactide (100 eq.) were charged in a small vial equipped with a Teflon-tight screw cap equipped with a magnetic stirrer. For solution polymerization of lactide, solvent ([M]$_0$=1M, THF, dichloromethane or toluene) added via syringe all at once was also charged in the vial. Aliquots were taken and analyzed by ^1H NMR sprectroscopy to estimate the conversion. The reaction mixture was finished by quenching with dichloromethane.
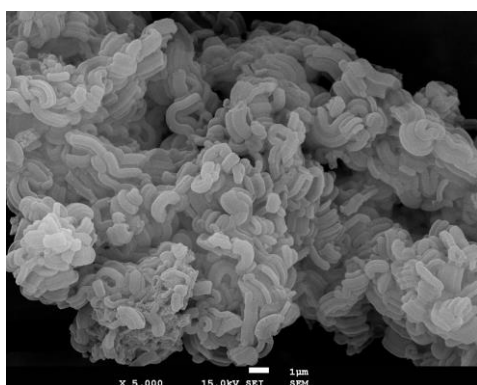
3. Results and Discussion

3.1 Titanium supported catalysts for ROP of LA
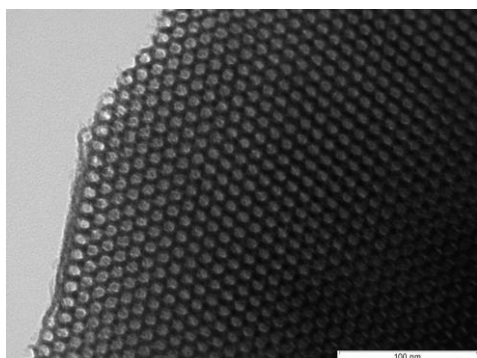
3.1.1 Characteristics of the support

Table 1 shows the surface area, pore volume, external area and pore diameter of SBA-15 and SEM and TEM pictures shown in **Fig.1** present the pores structures.

Table 1
Parameters of the mesoporous material used as support.

S_{BET} (m²/g)	V_p (cm³/g)	A_{ext} (m²/g)	D_p (Å)
743	1.12	87	70

(a)

(b)

Fig. 1 SEM (a) and TEM (b) pictures of SBA-15.

3.1.2 ROP of L-lactide with heterogeneous catalysts

The results obtained for the polymerization reactions of L-lactide using Ti(O^{i}Pr)$_4$/SBA-15 are shown in **Table 2**. Independently of the different sets of impregnation conditions used, the molar amounts of 0.54 and 0.76 mmol of titanium per gram of SBA-15 were grafted on the support. These amounts correspond to 2.5 (wt.%) and 3.5 (wt.%) of titanium in the catalyst. The catalysts having a higher amount of titanium led to a higher reaction yields (entries **1** and **2**). Based on the PLA yield, the conditions for the preparation of the catalyst performed during 1.5 hours at 50ºC were selected. Under these impregnation conditions, the influence of temperature of polymerization was studied. The reactions were studied at 50ºC, 70ºC, 90ºC and 110ºC. No polymer was obtained at 50ºC. The rate of the reactions increase with the temperature, until 90ºC, but there is no significant increase above that temperature. A similar yield was obtained for polymerization reactions carried out during 24h at 70ºC and during 4h at 90ºC. Run **14** shows that doubling up the LA/Ti molar ratio (200:1) the lactide is polymerized and the overall yields obtained are very similar (entries **12** *versus* **14**). Experiment **15** was performed for 48 hours with a second addition of the same amount of lactide after the first 24 hours, attaining a final LA/Ti molar ratio of 200:1. After the first 6 hours, the monomer conversion was determined by NMR analysis as 96%. After the additon of the second crop of lactide, the final PLA yield after plus 24 hours was 75%, which confirms that the second portion of lactide was also polymerized.

The results obtained for the polymerization reactions of L-lactide using TiCl(O^{i}Pr)$_3$/SBA-15 are shown in **Table 3**. Initial and final Ti/SBA-15 ratios show that, under the impregnation conditions used, all the titanium is effectively bonded to the support with exception of run **21** where the Ti/SBA-15 ratio was much higher (5mmol/g) and only 60% of metal was retained. Preparation of the catalyst at room temperature resulted in lower yields than those obtained with catalysts prepared at 50ºC – runs **20** *versus* **22**. The results obtained for the polymerizations reactions that used TiCl(O-*i*-Pr)$_3$/SBA-15 catalyst prepared during 1.5 hour and 50°C were not reproducible (entries **24** to **26**).

Table 2
Polymerization of L-LA using Ti(O^{i}Pr)$_4$/SBA-15.

Run	Impregnation conditions	Ti/SBA-15 (mmol/g)	Reaction conditions		Yield[c] (%)	M_n (g/mol)	M_w (g/mol)	PDI	T_m (ºC)
			T(ºC)	t(h)					
1[a]	3h, 50ºC	0.54	70	24	79	-	-	-	-
2[a]		0.76	70	24	87	5545	9684	1.75	162.3
5[a]	3h, RT	0.76	70	24	75	6841	10446	1.53	161.6
7[a]	1.5h, 50ºC	0.76	50	4	0	-	-	-	-
8[a]			70	4	51	-	-	-	-
9[a]			70	4	59	3485	5420	1.56	157.1
10[a]			90	4	75	-	-	-	-
11[a]			110	4	72	4589	8595	1.87	158.8
12[a]			70	24	77	3007	5708	1.90	159.4
14[b]			70	24	75	5335	9196	1.72	160.7
15[b]			70	24+24	75	3480	5995	1.72	163.5

[a]Polymerization conditions: LA/Ti=100:1
[b]Polymerization conditions: LA/Ti=200:1
[c]$(mass\ of\ polymer/mass\ of\ lactide) \times 100$

Table 3
Polymerization of L-LA using TiCl(O^{i}Pr)$_3$/SBA-15.

Run	Impregnation conditions	Ti/SBA-15 (mmol/g)		Yield[b] (%)	M_n (g/mol)	M_w (g/mol)	PDI	T_m (ºC)
		Initial	Final					
20	3h, 50ºC	0.76	0.76	85	5431	8949	1.65	157.9
21		5	3.05	90	-	-	-	-
22	3h, RT	0.76	0.76	70	4060	6414	1.58	155.5
24	1.5h, 50ºC	0.76	0.76	78	-	-	-	-
25				55	-	-	-	-
26				47	-	-	-	-

[a]Polymerization conditions: LA/Ti=100:1, temperature=70ºC, time= 24 h
[b]$(mass\ of\ polymer/mass\ of\ lactide) \times 100\%$

3.1.3 ROP of L-lactide with homogeneous catalysts

Ti(O-i-Pr)$_4$ and TiCl(O-i-Pr)$_3$ were tested for L-lactide polymerization. The yields in isolated PLA obtained are shown in **Table 4**. Despite both complexes catalyze the polymerization of lactide to PLA, Ti(O-i-Pr)$_4$ revealed to be a better catalyst than TiCl(O-i-Pr)$_3$. Ti(O-i-Pr)$_4$ revealed to be inactive at room temperature and at 70ºC, polymerization reactions using Ti(O-i-Pr)$_4$ as catalyst were completed after 2 hours. On the other hand, the reactions using TiCl(O-i-Pr)$_3$ as catalyst are slower, but a higher PLA yield was obtained after 24 hours. A plot of the lactide conversion versus time in the solution polymerization of L-lactide with Ti(O^{i}Pr)$_4$ (run **30**) and Ti(O^{i}Pr)$_4$/SBA-15 (runs **8** and **15**) is shown in **Fig.2**. Heterogeneous and homogeneous systems achieved the same monomer conversion, but the rate of polymerization with supported catalyst was slower than that of the homogeneous catalyst. The homogeneous reaction is fast and full conversion is reached after 2 hours, while for the heterogeneous catalyst, full conversion is reached after 6 hours.

3.1.4 Characteristics of the obtained polymers

Tables 2 to **4** shows the characteristics of the produced PLA samples. M_w values of the analyzed samples ranged from 5000 to 11000 g/mol and polydispersity index values from 1.5 to 1.9. Comparing both supported titanium alkoxido catalysts, polymers obtained with Ti(O-i-Pr)$_4$ presented higher molecular weights than polymers obtained using TiCl(O-i-Pr)$_3$.
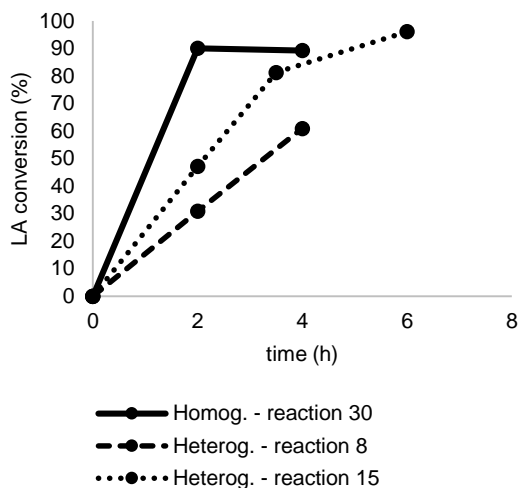
Fig. 2 L-lactide conversion as a function of reaction time for reactions 8, 15 and 30. Polymerization conditions: temp=70ºC, LA/Ti=100:1.

Table 4
Polymerization of L-LA using Ti(O^{i}Pr)$_4$ and TiCl(O^{i}Pr)$_3$.

| Catalyst | Run | Reaction conditions[a] | | Yield (%) | Tm (ºC) |
		T (ºC)	t (h)		
Ti(O^{i}Pr)$_4$	27	RT	2	-	-
	28		2	81	-
	30	70	4	70	-
	32		6	82	-
	35		24	80	159.3
TiCl(O^{i}Pr)$_3$	36	70	2	31	-
	37		24	89	-

[a]Polymerization conditions: LA/Ti=100:1.

Concerning the impregnation conditions, for both supported titanium compounds, higher molecular weights and the lowest PDI values obtained were achieved when the catalyst impregnation conditions were 3 hours and RT. In the case of using Ti(O^{i}Pr)$_4$/SBA-15, shorter impregnation times led to polymers with lower molecular weights and higher PDIs (run **2** and **12**). Higher molecular weight and PDI value was achieved for the polymer formed at higher polymerization temperature (run **9** and **11**). Using LA/Ti ratio of 200:1 instead of 100:1, the molecular weight is twice higher, and a lower PDI was achieved. The results for run **15** show that the molecular weights are similar to those achieved with LA/Ti=100:1 (run **14**). It can be concluded that when the first portion of lactide was converted the polymer

chains were terminated and after addition of a second crop of lactide new chains were initiated. The result revealed that the catalyst may be reused.

The melting temperatures ranged from 155 to 164ºC. Polymers samples **2** and **5** obtained with Ti(O^{i}Pr)$_4$/SBA-15 presented higher values of T$_m$ than polymers from samples **20** and **22** using TiCl(O^{i}Pr)$_3$/SBA-15, under the same impregnation conditions. Using Ti(O^{i}Pr)$_4$/SBA-15 catalyst, samples **2** and **5** present high melting temperatures, 162.3ºC and 161.6 ºC, respectively. It is thought that the higher molecular weight of the polymer produced by supported catalyst resulted in higher values of melting temperatures. Comparing melting temperatures of polymers obtained with Ti(O^{i}Pr)$_4$/SBA-15 and Ti(O^{i}Pr)$_4$, the homogeneous system did not reveal higher T$_m$ value.

3.2 Vanadium based catalysts for ROP of LA

Three different vanadium complexes were used in this work: VO(O^{i}Pr)[ONNO], VO(O^{i}Pr)$_3$ and V(NAda)(O^{i}Pr)$_3$. The structures are shown in **Fig. 3**. The results obtained for the ROP of *rac*-lactide in solution and in bulk using these catalysts are shown in Table 5. VO(O^{i}Pr)[ONNO] did not proved to be an appropriate catalyst for the ring-opening polymerization of lactide. Polymerization reactions carried out in DCM, THF and toluene solutions at RT, 60ºC and 90ºC, display practically null conversion. In bulk, at 130ºC, the system only attained 38% of monomer conversion was after 2h. Despite this low conversion value, a narrow molecular weight distribution was determined (PDI value near to 1). VO(O^{i}Pr)$_3$ is an efficient catalyst for the ROP of lactide in toluene solution. Total conversion is practically achieved after 8 hours (93%). However, VO(O^{i}Pr)$_3$ is much more active in bulk conditions, being the reaction completed after 15 minutes, which corresponds to 89% of conversion. The highest molecular weight (7726 g/mol) was observed for PLA obtained using this catalyst in toluene solution for 12 hours. PDI values remains between 1.0-1.3 in both conditions. V(NAda)(O^{i}Pr)$_3$ revealed to be active, but less than
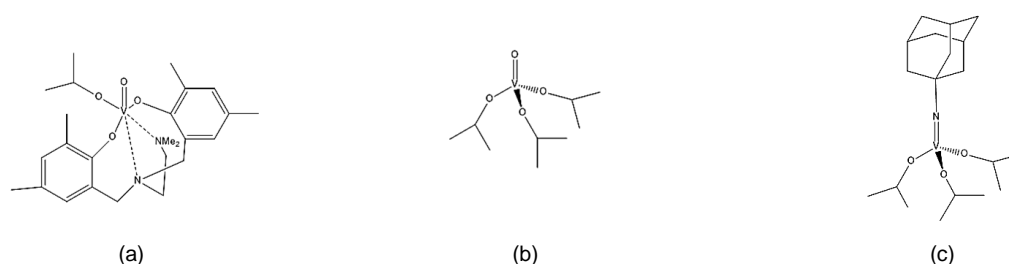
Fig. 3 Structures of the vanadium complexes: (a) VO(O^{i}Pr)[ONNO], (b) VO(O^{i}Pr)$_3$, (c) V(NAda)(O^{i}Pr)$_3$

Table 5
Polymerization of rac-LA using VO(O^{i}Pr)[ONNO] and LA/catalyst=100:1.

Catalyst	Run	Solvent	T (ºC)	t (h)	Conversion[a] (%)	M$_n$[b] (g/mol)	M$_{n(theo)}$[c] (g/mol)	PDI[b]
VO(O^{i}Pr)[ONNO],	39	DCM	RT	18	1	-	-	-
	40	THF	60	4	0	-	-	-
	41	toluene	90	4	2	-	-	-
	42	toluene	100	18	26	-	-	-
	43	bulk	130	2	38	2272	5477	1,13
VO(O^{i}Pr)$_3$	49	toluene	90	4	47	2024	2258	1,07
	51			6	72	3155	3459	1,09
	53			8	93	6910	4468	1,21
	55			12	92	7726	4420	1,14
	56			16	95	-	-	-
	57			18	91	5210	4372	1,27
	59	bulk	130	2 min	2	-	-	-
	60			5 min	24	1424	1153	1,09
	62			7 min	52	3030	2498	1,12
	63			10 min	79	3334	3795	1,16
	64			15 min	89	4841	4276	1,25
	66			30 min	90	4983	4324	1,29
	67			1h	93	5558	4420	1,26
V(NAda)(O^{i}Pr)$_3$	69	toluene	90	2	8	-	-	-
	71			4	36	3598	1730	1,18
	75			6	44	3920	2114	1,17
	78			8	70	5896	3363	1,11
	81			16	79	5446	3795	1,12
	83			18	89	4043	4276	1,23
	84	bulk	130	2	51	3116	2450	1,14

[a]Determined by ^{1}H NMR analysis
[b]Determined from GPC analysis
[c]Calculated according to the conversion (MLA=144.13g/mol)

the analogous oxo-complex. Full conversion was reached after 18h hours, in toluene, at 90ºC. The system showed to be more active in bulk conditions, despite the lower M$_n$ value obtained. PDI values ranging from 1.1-1.3 were observed.

If the polymerization rate is a first order reaction for the monomer:

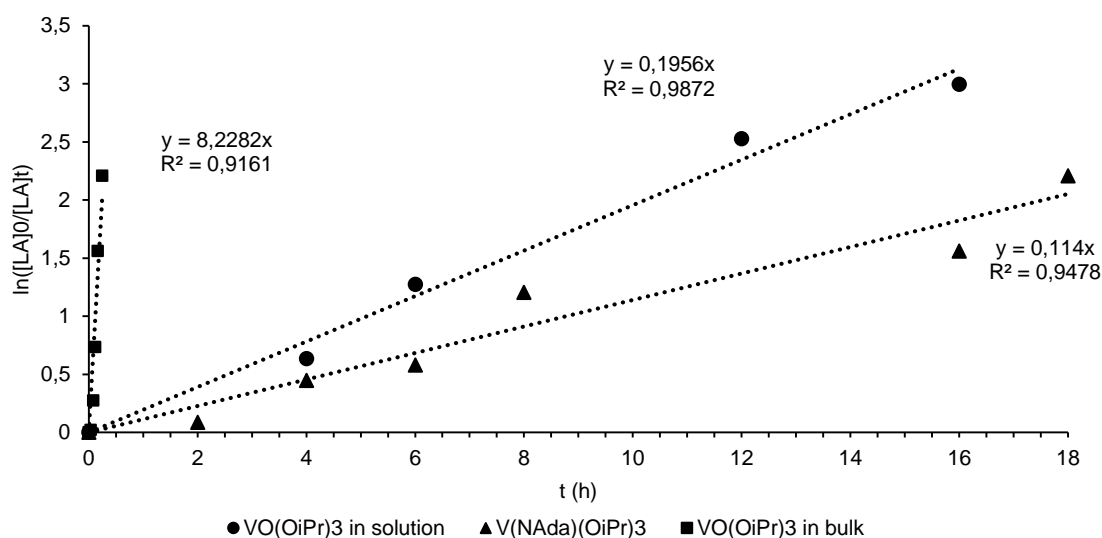$$\ln\left(\frac{[LA]_0}{[LA]_t}\right) = kt \qquad \textbf{Eq.1}$$

where k is the reaction rate constant in [time^{-1}], t is time, $[LA]_0$ is the lactide concentration at t=0, $[LA]_t$ is the lactide concentration at time t. And where $[LA]_0/[LA]_t$ is calculated attending the definition of conversion:

$$[LA]_0/[LA]_t = \frac{1}{1-conv} \qquad \textbf{Eq.2}$$

The conversion profiles of L-lactide to time, shown in **Fig.4**, respectively, reveal first order reactions. **Fig.4** highlights the higher activity of $VO(O^iPr)_3$ in relation to $V(NAda)(O^iPr)_3$ and also a much higher polymerization rate in bulk conditions.

$VO(O^iPr)_3$ and $V(NAda)(O^iPr)_3$ catalysts give rise to racemization of lactide and originate the formation of *meso*-lactide. The presence of *meso*-lactide was identified by ^{1}H NMR. In general, it was thought that the formation of meso-LA increases with the increasing of reaction time. The formation of *meso*-LA was not observed when instead of using *rac*-lactide, polymerizations of L-lactide were performed and a LA/catalyst ratio of 500:1 in bulk conditions was used. In these conditions, a conversion of 68% and a PDI very close to 1 were obtained with catalyst $V(NAda)(O^iPr)_3$ for 2 hours, at 130ºC.

$y = 0,1956x$
$R^2 = 0,9872$

$y = 8,2282x$
$R^2 = 0,9161$

$y = 0,114x$
$R^2 = 0,9478$

ln([LA]0/[LA]t)

t (h)

● VO(OiPr)3 in solution   ▲ V(NAda)(OiPr)3   ■ VO(OiPr)3 in bulk

Fig. 4 *Rac*-lactide conversion as function of reaction time for $VO(O^iPr)_3$ in toluene at 90ºC and in bulk for 130ºC and for $V(NAda)(O^iPr)_3$ in toluene at 90ºC. Polimerization conditions: *rac*-LA/Ti=110:1

4. Concluding Remarks

Titanium supported catalyst were prepared by reacting $Ti(O-i-Pr)_4$ or $TiCl(O-i-Pr)_3$ with pretreated SBA-15. Lactide polymerization was conducted with titanium alkoxido supported catalysts in different conditions. The increasing of impregnation time did not lead to significant differences in PLA yields. However, in the case of using $Ti(O^iPr)_4$/SBA-15, shorter impregnation times led to polymers with lower molecular weights and higher PDIs (run **2** and **12**), suggesting that different active species are formed. Similar yields were obtained for polymerization reactions carried out during 24h at 70ºC and during 4 hours at 90ºC. The rate of the reactions increased with the temperature, until 90ºC, but there is no significant increase above that temperature. M_n values do not follow the increasing of yield with the time, and that the highest PDI value was obtained for 24 hours reaction. Having in mind that for polymers obtained with supported $Ti(O^iPr)_4$ full conversion is reached after 6 hours, a higher PDI value suggests that during the polymerization time in which monomer concentration is very low, secondary reactions may occur. This could explain the variations in molecular weight and the highly broad molecular weight distribution (run **9** and **12**).

An experiment with two sequential additions of lactide (200:1) was performed and the determination of the molecular weights of samples **12**, **14** and **15** did not confirm that the system was "living", because the molecular weight of the polymer did not increase to the double, but it showed that the system could

be reused, which means that the catalyst did not deactivate.

Lactide polymerization was conducted also with the analogous homogeneous systems. Supported and homogeneous systems achieved the same monomer conversion, the activity of the supported catalyst was lower than that of the homogeneous catalysts. The mass transfer limitation of the monomer may be responsible for the difference in the polymerization rates.

Vanadium catalysts were tested in the polymerization of *rac*-lactide polymerization was conducted with. $VO(O^iPr)[ONNO]$ did not proved to be active in the ring-opening polymerization of lactide, maybe due to stereochemical reasons. $VO(O^iPr)_3$ revealed to be very active in the ROP of lactide in solution, and even more in bulk conditions. In both cases, the similarity between corrected and theoretical molecular weights of the samples indicates that there are three PLA chains initiated by the three isopropoxido groups of the catalyst. $V(NAda)(O^iPr)_3$ is active in the ROP of lactide, but less than the analogous oxo-complex. . This difference in activity is probably caused by the higher acidity of vanadium metal center in $VO(O^iPr)_3$ and the robustness of oxo-vanadium complexes. Vanadium catalysts used in ROP of lactide lead to low PDI values ranging 1.1 and 1.3, indicating a good control of polymerization.

$VO(O^iPr)_3$ and $V(NAda)(O^iPr)_3$ catalysts originate *meso*-LA. This may be avoid if the LA/catalyst ratio was increased to 500:1 in bulk conditions, leading to a stereoregular polymer with higher molecular weight and lower PDI.

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