J. Braz. Chem. Soc., Vol. 26, No. 11, S1-S4, 2015.
Printed in Brazil - ©2015 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Supplementary Information

Catalytic Activity of a Titanium(IV)/Iron(II) Heterometallic Alkoxide in the Ring-Opening Polymerization of ε-Caprolactone and *rac*-Lactide

Siddhartha O. K. Giese, Cristiano Egevardt, André Luis Rüdiger, Eduardo L. Sá, Thiago Alessandre Silva, Sônia F. Zawadzki, Jaísa F. Soares and Giovana G. Nunes*

Departamento de Química, Universidade Federal do Paraná (UFPR), 81530-900 Curitiba-PR, Brazil

Table S1. Solution polymerization of ε-caprolactone at 90 °C with [FeCl{$Ti_2(OPr^i)_9$}] (**1**) as initiator, with an initial monomer/initiator (ε-CL/**1**) ratio of 500 and sucessive additions of monomer to the reaction mixture

	ε-CL / mL	time / h	α_c / %	Yield[a] / %	M_n(GPC)[b] / (g mol^{-1})	PDI[c]
Reaction mixture	0.5	8	99	99	9100	1.60
1st addition	+0.5	8	99	99	15400	1.60
2nd addition	+0.5	8	90	75	14000	1.51
3rd addition	+0.5	8	40	50	13000	1.52

[a]Yield based on the isolated amount of solid; [b]average molecular weights (M_n) determined by GPC in the and multiplied by the correction value of 0.56;[27] [c]polydispersity index, also calculated from GPC data.

Table S2. In bulk polymerization of ε-caprolactone (ε-CL) with [$Ti(OPr^i)_4$] as initiator. The εCL/**2** ratio was fixed at 250

entry	Temperature / °C	time / min	α_C / %	Yield[a] / %	M_n(theoretical)[b] / (g mol^{-1})	M_n (^{1}H RMN)[c] / (g mol^{-1})	M_n(GPC)[d] / (g mol^{-1})	PDI[e]	N_n[f]
1	30	1440	100	93	33385	7990	7400	1.49	4.50
2	60	60	99	94	35098	6848	7750	1.66	4.53
3	90	30	96	80	34242	7876	7490	1.67	4.57
4	90	60	99	93	35098	7762	7410	1.66	4.73
5	120	30	100	99	35098	8104	7850	1.68	4.47
6	120	60	100	95	33956	9702	7680	1.67	4.42

[a]Yield based on the amount of isolated solid; [b]theoretical molecular weight calculated from the formula: [$M_{W(CL)}$ × (CL/**1**) × α_c] + 60 (for the terminal groups); [c]average molecular weights determined by ^{1}H NMR; [d]average molecular weights (M_n) determined by GPC in the using the correction value 0.56;[27] [e]polydispersity index, also calculated by GPC; [f]calculated from M_n(theoretical)/M_n(GPC). It refers to the number of growing chains *per* molecule of the initiator.

*e-mail: nunesgg@ufpr.br

Table S3. Polymerization of ε-caprolactone (ε-CL) in toluene solution (entries 1 and 2) and toluene/isopropanol 10:1 (entries 3 to 6) with $[FeCl_2(Pr^iOH)_4]$ (**4**) as initiator

entry	ε-CL/Initiator[a]	Temperature / °C	time / min	Yield[b] / %	M_n(GPC)[c] / (g mol^{-1})	PDI[d]
1	500	90	8	–	–	–
2	500	90	20	20	1690	1.10
3	250	85	20	73	980	2.04
4	500	85	20	100	1060	1.09
5	1000	85	20	100	1200	1.05
6	2000	85	20	100	1230	1.24

[a]Yield based on the amount of isolated solid; [b]theoretical molecular weight, calculated for quantitative conversions from the formula: $M_{CL} \times ([CL] / [\mathbf{1}]) \times$ conversion + 60 (for the terminal groups); [c]average molecular weights (M_n) determined by GPC in tetrahidrofuran using the correction value 0.56;[27] [d]polydispersity index (PDI), calculated from M_n(theoretical)/M_n(GPC).

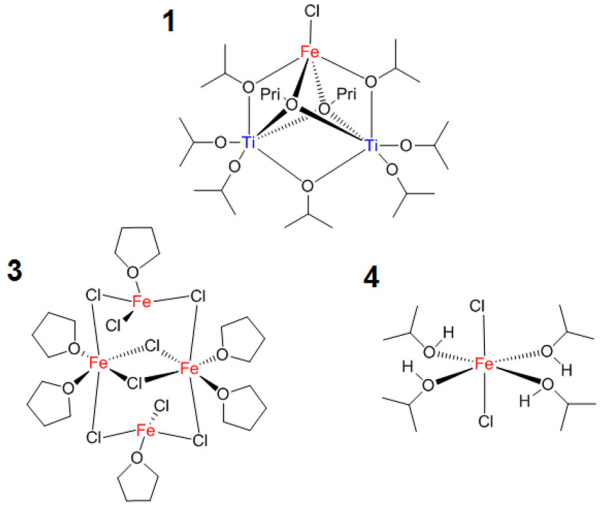

Figure S1. Structural representation of the complexes $[FeCl\{Ti_2(OPr^i)_9\}]$ (**1**), $[Fe_4Cl_8(thf)_6]$ (**3**) and $[FeCl_2(Pr^iOH)_4]$ (**4**), employed in this work as initiators for ε-caprolactone and *rac*-lactide polymerization.

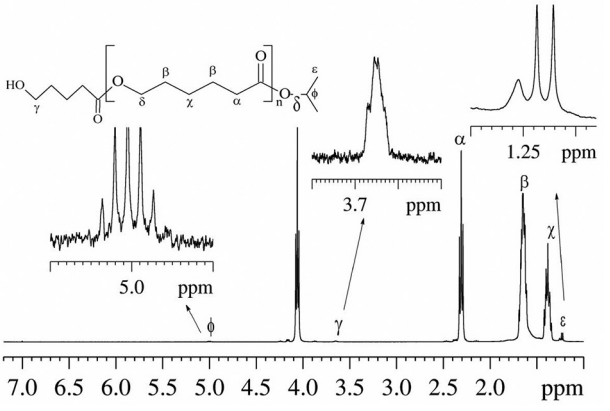

Figure S2. ^{1}H NMR spectrum (400.13 MHz, $CDCl_3$) recorded for poly(ε-caprolactone).

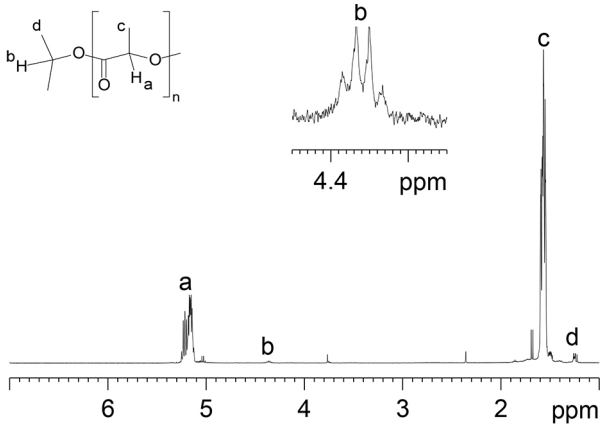

Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) for poly(*rac*-lactide).

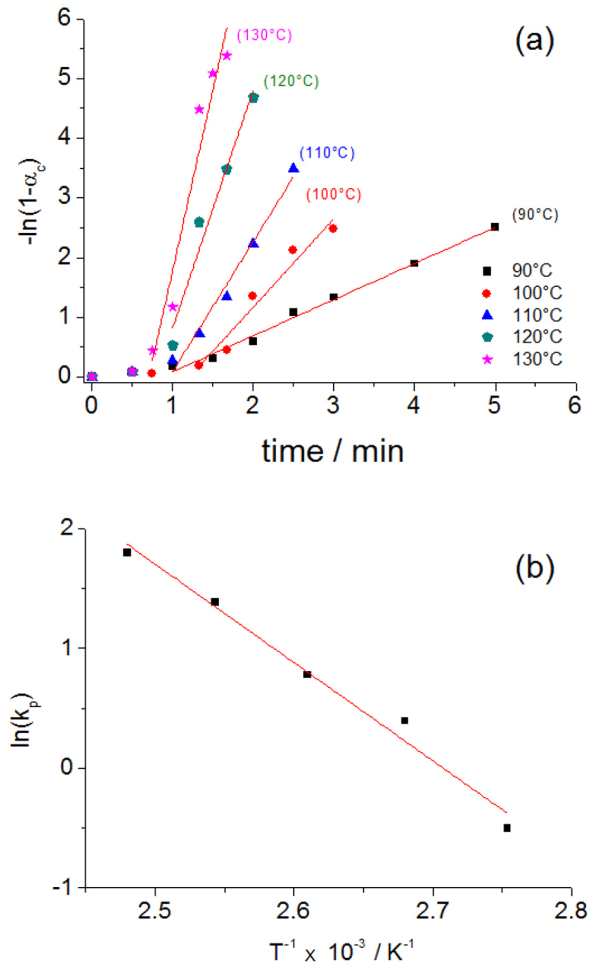

Figure S4. Kinetic plots for consumption of ε-caprolactone *versus* time at 90, 100, 110 and 120 and 130 °C for an ε-CL/[Ti(OPr^i)$_4$] ratio of 250 in (a) and plot of ln k_p *versus* 1/T for ε-caprolactone polymerization in an ε-CL/[Ti(OPr^i)$_4$] molar ratio of 250 in (b).

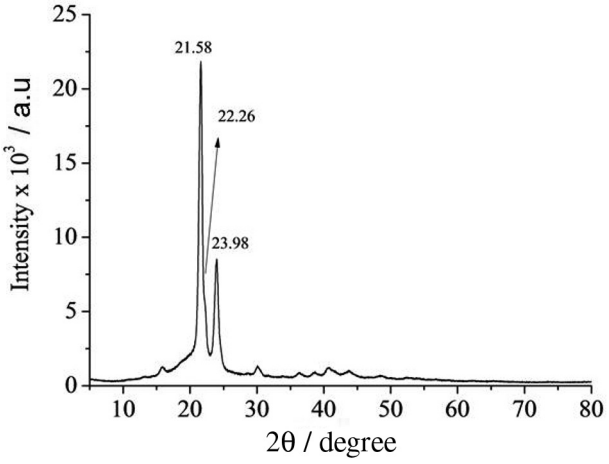

Figure S5. Powder X-ray diffraction pattern registered for a typical poly(ε-caprolactone) sample produced in this work.

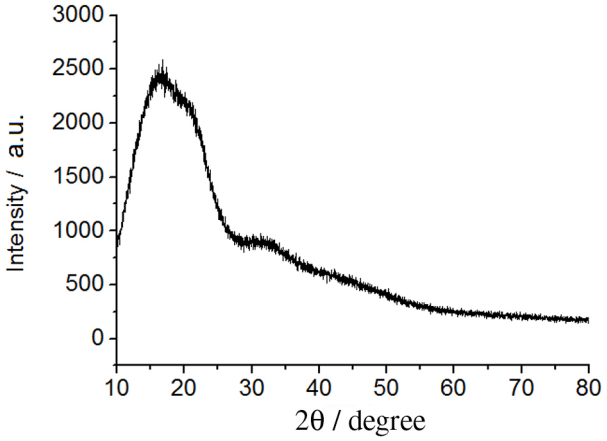

Figure S6. Powder X-ray diffraction pattern recorded for a representative poly(*rac*-lactide) sample produced in this work.

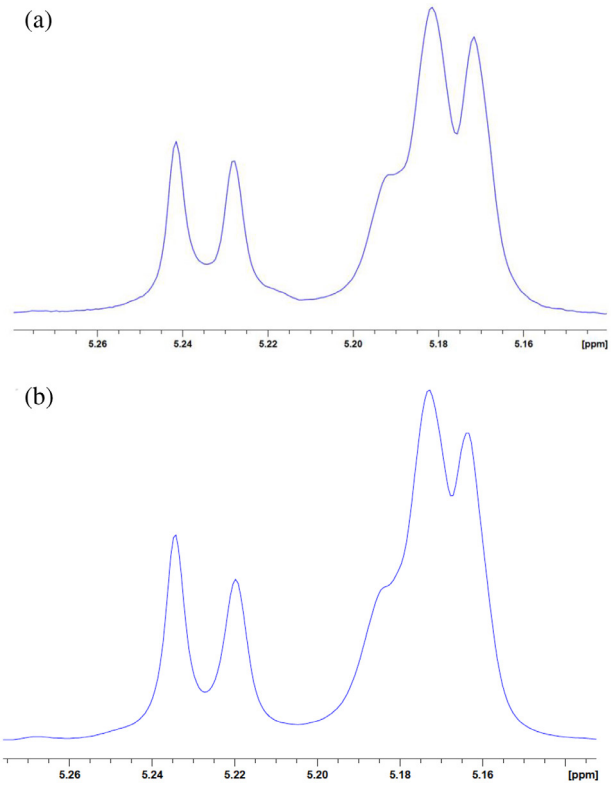

Figure S7. Homodecoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$) registered for the methyne region of poly(*rac*-lactide) using **1** as initiator in (a) or **2** as initiator in (b).

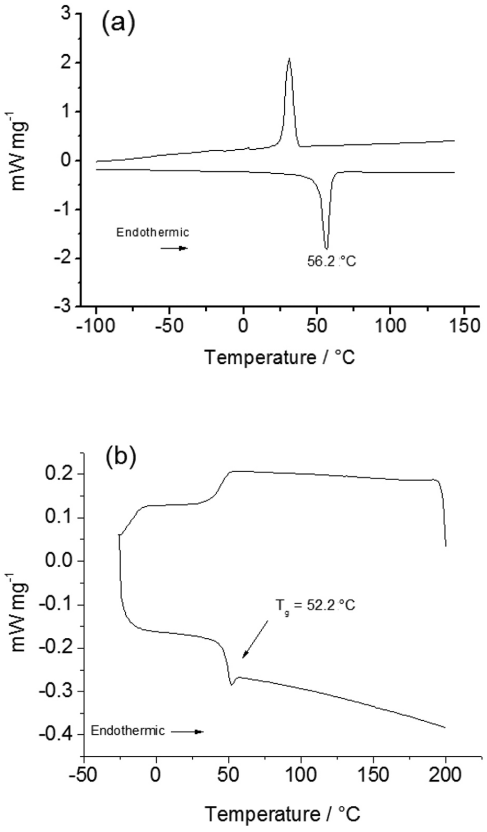

Figure S8. Typical DSC curve for poly(ε-caprolactone) analyzed from ambient temperature to 150 °C, then left for 5 min in isotherm, cooled to −120 °C, 5 min in isotherm and heated up again to 150 °C at a scan rate of 10 °C min^{-1} in (a); and poly(*rac*-lactide) analyzed from −20 to 200 °C, left for 5 min in isotherm, cooled to −20 °C, 5 min in isotherm and heated up again to 200 °C at a scan rate of 10 °C min^{-1} in inert atmosphere in (b).

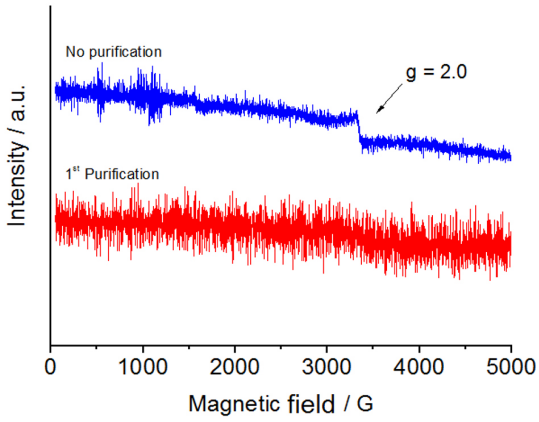

Figure S9. X-Band EPR spectra of ε-PCL prepared with **1** as initiator, registered at 77K for the original sample and for the solid obtained after reprecipitation.