Supporting information for: High level potential energy surface and mechanism of the Al(CH₃)₂OCH₃ promoted lacton polymerization. Initiation and Propagation

Stefan Vogt Geisse, Ricardo A. Mata, and Alejandro Toro-Labbé

E-mail:

Tables

Table S1: Thermodynamic corrections for the glycolide initiation reaction

Method	Cat+mon	r	ts1	i1	ts2	i2	ts3	р
S_vib	0.0	4.6	2.86	2.83	1.96	2.32	1.76	3.21
H_correct	0.0	-0.58	-0.72	-0.72	-1.18	-0.32	-0.61	-0.47
$H_{-}TS$	0.0	-5.17	-3.58	-3.55	-3.15	-2.64	-2.37	-3.68
ZPVE_correct	0.0	1.17	1.17	2.28	2.32	2.39	1.97	1.89
$Solvent_Correction (THF)$	0.0	11.3	13.13	11.81	7.6	11.39	12.8	12.33
Solvent_Correction (Tolune)	0.0	6.4	7.45	6.63	4.24	6.41	7.22	6.98

Figures

Method	Cat+mon	r	ts1	i1	ts2	i2	ts3	р
S_vib	0.0	4.48	2.28	2.79	2.19	2.43	2.02	3.88
$H_{-}correct$	0.0	-0.05	-0.4	-0.12	-1.09	-0.25	-0.49	0.35
$H_{-}TS$	0.0	-4.53	-2.67	-2.91	-3.28	-2.68	-2.51	-3.52
$ZPVE_correct$	0.0	1.32	1.65	2.04	2.02	2.17	1.66	1.62
Solvent_Correction (THF)	0.0	12.38	12.87	12.0	8.33	11.87	11.84	11.83
Solvent_Correction (Toluene)	0.0	6.99	7.26	6.77	4.63	6.73	6.71	6.71

Table S2: Thermodynamic data for the dxo initation reaction

Table S3: Thermodynamic data for the ϵ -caprolactone initiation reaction

Method	Cat+mon	r	ts1	i1	ts2	i2	ts3	р
S_vib	0.0	4.4	1.98	2.84	2.37	2.2	1.82	2.63
$H_{-}correct$	0.0	-0.62	-0.51	-0.64	-1.6	-0.32	-0.55	-0.21
$H_{-}TS$	0.0	-5.02	-2.49	-3.48	-3.97	-2.52	-2.37	-2.84
ZPVE_correct	0.0	1.19	1.59	1.7	1.73	2.08	1.49	1.31
$Solvent_Correction(THF)$	0.0	10.88	12.73	12.32	11.71	11.65	12.6	10.0
Solvent_Correction(Toluene)	0.0	6.13	7.17	6.95	6.52	6.59	7.14	5.65

Table S4: Thermodynamic data for the glycolide propagation reaction

Cat+mon	r	ts1	i1	ts2	р
0.0	6.27	3.88	3.62	3.17	4.64
0.0	-0.55	-1.03	-0.49	-0.61	0.03
0.0	-6.82	-4.9	-4.11	-3.78	-4.61
0.0	0.95	1.47	2.45	1.19	1.65
0.0	3.35	3.18	4.55	2.08	2.25
0.0	1.89	1.81	2.58	1.33	1.44
	$\begin{array}{c} {\rm Cat}{\rm +mon} \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \end{array}$	Cat+monr0.06.270.0-0.550.0-6.820.00.950.03.350.01.89	$\begin{array}{rrrr} Cat+mon & r & ts1 \\ 0.0 & 6.27 & 3.88 \\ 0.0 & -0.55 & -1.03 \\ 0.0 & -6.82 & -4.9 \\ 0.0 & 0.95 & 1.47 \\ 0.0 & 3.35 & 3.18 \\ 0.0 & 1.89 & 1.81 \end{array}$	$\begin{array}{cccccc} {\rm Cat+mon} & {\rm r} & {\rm ts1} & {\rm i1} \\ \\ 0.0 & 6.27 & 3.88 & 3.62 \\ 0.0 & -0.55 & -1.03 & -0.49 \\ 0.0 & -6.82 & -4.9 & -4.11 \\ 0.0 & 0.95 & 1.47 & 2.45 \\ 0.0 & 3.35 & 3.18 & 4.55 \\ 0.0 & 1.89 & 1.81 & 2.58 \end{array}$	$\begin{array}{ccccccc} Cat{+}mon & r & ts1 & i1 & ts2 \\ 0.0 & 6.27 & 3.88 & 3.62 & 3.17 \\ 0.0 & -0.55 & -1.03 & -0.49 & -0.61 \\ 0.0 & -6.82 & -4.9 & -4.11 & -3.78 \\ 0.0 & 0.95 & 1.47 & 2.45 & 1.19 \\ 0.0 & 3.35 & 3.18 & 4.55 & 2.08 \\ 0.0 & 1.89 & 1.81 & 2.58 & 1.33 \end{array}$

Table S5: Thermodynamic data for the dxo propagation reaction

Method	Cat+mon	r	ts1	i1	ts2	р
S_vib	0.0	5.61	3.69	3.6	2.86	5.26
H_correct	0.0	-1.34	-1.63	-1.62	-0.74	-0.32
$H_{-}TS$	0.0	-6.96	-5.32	-5.22	-3.6	-5.59
ZPVE_correct	0.0	0.99	0.96	2.17	1.37	1.53
$Solvent_Correction(THF)$	0.0	3.65	4.82	5.94	3.7	4.68
Solvent_Correction(Toluene)	0.0	2.1	2.76	3.39	2.2	2.73

Cat+mon	r	ts1	i1	ts3	\mathbf{p}
0.0	6.68	5.86	5.88	5.13	7.34
0.0	-0.81	-1.25	-0.69	-1.73	-0.59
0.0	-7.49	-7.11	-6.56	-6.85	-7.93
0.0	0.97	0.28	1.47	0.27	0.72
0.0	4.95	4.68	4.32	5.74	4.52
0.0	2.83	2.63	2.38	3.23	2.54
	$\begin{array}{c} \text{Cat+mon} \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \end{array}$	$\begin{array}{ccc} {\rm Cat+mon} & {\rm r} \\ 0.0 & 6.68 \\ 0.0 & -0.81 \\ 0.0 & -7.49 \\ 0.0 & 0.97 \\ 0.0 & 4.95 \\ 0.0 & 2.83 \end{array}$	$\begin{array}{cccc} {\rm Cat+mon} & {\rm r} & {\rm ts1} \\ 0.0 & 6.68 & 5.86 \\ 0.0 & -0.81 & -1.25 \\ 0.0 & -7.49 & -7.11 \\ 0.0 & 0.97 & 0.28 \\ 0.0 & 4.95 & 4.68 \\ 0.0 & 2.83 & 2.63 \end{array}$	$\begin{array}{c ccccc} {\rm Cat+mon} & {\rm r} & {\rm ts1} & {\rm i1} \\ \hline 0.0 & 6.68 & 5.86 & 5.88 \\ \hline 0.0 & -0.81 & -1.25 & -0.69 \\ \hline 0.0 & -7.49 & -7.11 & -6.56 \\ \hline 0.0 & 0.97 & 0.28 & 1.47 \\ \hline 0.0 & 4.95 & 4.68 & 4.32 \\ \hline 0.0 & 2.83 & 2.63 & 2.38 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table S6: Thermodynamic data for the ϵ -caprolactone propagation reaction



Figure S1: Two-dimensional potential energy surface in terms of the Al-O3 bond distance and the C1-Al-O2-C2 dihedral angle. An extended potential energy plateau is present, through which the reaction advances. In the flattest region of the PES the energy difference is lower then 0.5 kcal mol⁻¹.