Supporting information for: High level potential energy surface and mechanism of the $Al(CH_3)_2OCH_3$ promoted lacton polymerization. Initiation and Propagation

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Tables

Table S1: Thermodynamic corrections for the glycolide initation reaction

Method	Cat+mon	r	ts1	i1	ts2	i2	ts3	p
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

Table S2: Thermodynamic data for the dxo initation reaction

Method	Cat+mon	r	ts1	i1	ts2	i2	ts3	p
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 S3: Thermodynamic data for the ϵ-caprolactone initation reaction

Method	Cat+mon	r	ts1	i1	ts2	i2	ts3	p
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

Method	Cat+mon	r	ts1	i1	ts2	p
S_vib	0.0	6.27	3.88	3.62	3.17	4.64
H_correct	0.0	-0.55	-1.03	-0.49	-0.61	0.03
H_TS	0.0	-6.82	-4.9	-4.11	-3.78	-4.61
ZPVE_correct	0.0	0.95	1.47	2.45	1.19	1.65
Solvent_Correction(THF)	0.0	3.35	3.18	4.55	2.08	2.25
Solvent_Correction(Toluene)	0.0	1.89	1.81	2.58	1.33	1.44

Table S5: Thermodynamic data for the dxo propagation reaction

Method	Cat+mon	r	ts1	i1	ts2	p
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

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

Method	Cat+mon	r	ts1	i1	ts3	p
S_vib	0.0	6.68	5.86	5.88	5.13	7.34
H_correct	0.0	-0.81	-1.25	-0.69	-1.73	-0.59
H_TS	0.0	-7.49	-7.11	-6.56	-6.85	-7.93
ZPVE_correct	0.0	0.97	0.28	1.47	0.27	0.72
Solvent_Correction(THF)	0.0	4.95	4.68	4.32	5.74	4.52
Solvent_Correction(Toluene)	0.0	2.83	2.63	2.38	3.23	2.54

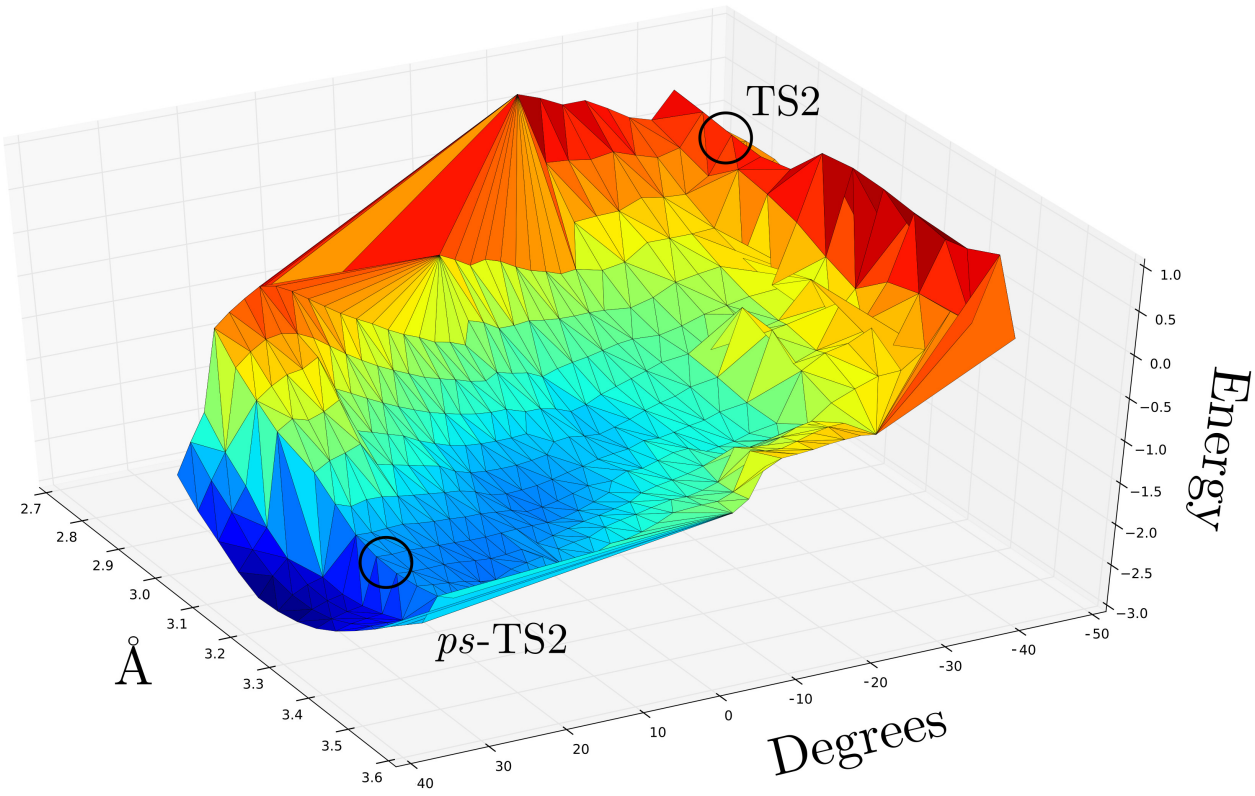

Figure S1: Two-dimensional potential energy surface in terms of the Al-O3 bond distance and the C1-Al-O2-C2 dihedral angle. An extended potential energy plateau is present, through which the reaction advances. In the flattest region of the PES the energy difference is lower then 0.5 kcal mol^{-1}.