Supplementary Information

Effects of Nucleophilic Ligands on the Chain Initiation Efficiency of Po-lar Monomer Polymerizations Catalyzed by 2-Methoxyethylaminobis(phenolate)yttrium Complexes: A DFT Study

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Table S1. Selected bond distances (Å) and angles (degree) in the B3LYP-optimized complexes 1a,and the X-ray data of 1a.



Bond	X-ray Data	B3LYP	Δ	Angle	X-ray Data	B3LYP	Δ
Y1-O3	2.127	2.171	0.044	03-Y1-01	153.40	151.33	2.07
Y1-01	2.131	2.172	0.041	O3-Y1-O4	85.00	86.93	1.93
Y1-O4	2.350	2.422	0.072	01-Y1-O4	86.18	86.08	0.10
Y1-O2	2.425	2.479	0.054	O3-Y1-O2	91.71	89.84	1.87
Y1-N1	2.576	2.671	0.095	01-Y1-O2	89.95	91.29	1.34
				O4-Y1-O2	164.08	168.01	3.93
				O3-Y1-C22	104.78	105.61	0.83
				O1-Y1-C22	101.82	103.05	1.23
				O4-Y1-C22	107.62	106.01	1.61
				O2-Y1-C22	88.31	85.98	2.33
				O3-Y1-N1	78.63	76.87	1.76
				01-Y1-N1	77.44	77.20	0.24
				O4-Y1-N1	96.12	100.78	4.66
				O2-Y1-N1	67.97	67.24	0.73
				C22-Y1-N1	156.22	153.17	3.05
Average error			0.061	Average error			1.85

 $\label{eq:second} \begin{array}{l} \textbf{Table S2. Selected bond distance (Å) and angles (degree) in the B3LYP-optimized complexes 1b, \\ and the X-ray data of 1b. \end{array}$



Bond	X-ray Data	B3LYP	Δ	Angle	X-ray Data	B3LYP	Δ
Y1-O27	2.145	2.173	0.028	O27-Y1-O17	153.98	151.84	2.14
Y1-017	2.157	2.174	0.017	O27-Y1-N2	101.88	105.39	3.51
Y1-N2	2.276	2.288	0.012	O17-Y1-N2	103.63	102.73	0.90
Y1-O31	2.355	2.429	0.074	O27-Y1-O31	83.99	84.29	0.30
Y1-O4	2.414	2.461	0.047	O17-Y1-O31	84.71	87.16	2.45
Y1-N1	2.533	2.675	0.142	N2-Y1-O31	104.34	104.60	0.26
				O27-Y1-O4	96.41	88.41	8.00
				O17-Y1-O4	85.26	89.17	3.91
				N2-Y1-O4	98.03	98.27	0.24
				O31-Y1-O4	157.10	157.09	0.01
				O27-Y1-N1	77.08	76.17	0.91
				O17-Y1-N1	79.52	77.03	2.49
				N2-Y1-N1	165.81	165.56	0.25
				O31-Y1-N1	89.71	89.83	0.12
				O4-Y1-N1	68.24	67.33	0.91
				Si2-N2-Si1	127.15	122.91	4.24
				Si2-N2-Y1	118.45	121.66	3.21
				Si1-N2-Y1	113.59	115.42	1.83
Average error			0.053	Average error			1.98

Scheme S1. Energy profile for isomerization of complexes 5a-5c (energy in kcal/mol).



It is noted that a transition state with an energy barrier of 14.3 kcal/mol was located for the conversion of **5a** to **INT1a**. However, attempts to locate analogous transition states for the cases of **5b** and **5c** were fruitless. It is also noteworthy that the process of isomerization of **5b** is somewhat different from the case of **5a** and **5c** since the $-N(SiHMe_2)_2$ is bulkier than $-CH_2SiHMe_2$ and -OiPr. In the case of **5a** and **5c**, species **5** transformed to **INT1** by carbonyl oxygen de-coordination. **INT1** subsequently transformed to **6** through **TS**^{iso}, with the energy barrier of 16.8 kcal/mol (**TS**^{iso} **a**) and 14.9 kcal/mol (**TS**^{iso} **c**). In the case of **5b**, The species **5** transformed to **INT1b** and **INT2b** by carbonyl oxygen de-coordination. **INT2b** subsequently converted to **INT3b** through **TS**^{iso}**b**. Finally, the carbonyl oxygen re-coordinate to Y center via **TS**[**INT3b-6b**].



Scheme S2. Insertion of the second BBL molecule catalyzed by complexes 1a-1c.

Species a	$\Delta G^{\ddagger}_{ m sol}$	Species b	$\Delta G^{\ddagger}_{ m sol}$	Species c	$\Delta G^{\ddagger}_{ m sol}$
ба	0.0	6b	0.0	6с	0.0
11a ^{syn}	4.8	11b ^{syn}	4.1	11c ^{syn}	3.5
TS[11a-12a] ^{syn}	20.8	TS[11b-12b] ^{syn}	17.8	TS[11c-12c] ^{syn}	17.8
12a ^{syn}	14.6	12b ^{syn}	10.8	12c ^{syn}	12.2
TS[12a-13a] ^{syn}	18.9	TS[12b-13b] ^{syn}	14.2	TS[12c-13c] ^{syn}	15.7
13a ^{syn}	13.5	13b ^{syn}	8.6	13c ^{syn}	10.2
14a ^{syn}	-0.1	14b ^{syn}	-2.2	14c ^{syn}	-4.6
6a	0.0	6b	0.0	6с	0.0
11a ^{iso}	4.8	11b ^{iso}	6.7	11c ^{iso}	4.1
TS[11a-12a] ^{iso}	18.7	TS[11b-12b] ^{iso}	17.1	TS[11c-12c] ^{iso}	16.5
12a ^{iso}	16.9	12b ^{iso}	11.2	12c ^{iso}	12.0
TS[12a-13a] ^{iso}	22.6	TS[12b-13b] ^{iso}	23.2	TS[12c-13c] ^{iso}	18.7
13a ^{iso}	1.5	13b ^{iso}	0.9	13c ^{iso}	-2.1
14a ^{iso}	-1.4	14b ^{iso}	-1.7	14c ^{iso}	-4.5

Table S3. The calculated free energy in solution (kcal/mol) for the stationary points involved in the reaction of the second monomer shown in Scheme S2.

The results indicate that the syndiotactic pathway is more favorable and all the energy barriers in the case of 1a - 1c are lower than that for chain initiation (20.8, 17.8, and 17.8 kcal/mol *vs* 26.2, 27.0, and 21.7 kcal/mol, respectively).



Figure S1. Relaxed PES scan for the Y1–O2 distance (step size = 0.1 Å, number of step = 25) of **1a**, **1b**, and **1c** at the B3LYP/6-31G(d) \cap SDD level.



Figure S2. Relaxed PES scan for the Y1–O3 distance (step size = 0.1 Å, number of step = 25) of **2a**, **2b**, and **2c** at the B3LYP/6-31G(d) \cap SDD level.



Figure S3. Relaxed PES scan for the Y1–N2 distance (step size = 0.1 Å, number of step = 25) of **7a**, **7b**, and **7c** at the B3LYP/6-31G(d) \cap SDD level.

It is noted that there are inflection points on the potential energy surfaces shown in Figures S1 and S3, which may indicate the transition state region. However, attempts to locate transition state by taking such inflection points as initial structures were fruitless.