Electronic Supplementary Information for:

Screening of Metal Complex Catalysts Using Bidentate Schiff Base Ligands for Controlled Cationic Polymerization of Vinyl Ethers Using *In Situ* Complexation Method

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Contents:

Experimental Section

Synthesis

N-Phenyl-3,5-di-*tert*-butylsalicylideneamine (1)

Aniline (0.94 g, 101 mmol) was added to a methanol solution of 3,5-di-*tert*-butylsalicylaldehyde (2.37 g, 101 mmol) while stirring under a nitrogen atmosphere at room temperature. The mixed solution was refluxed for 6 h, and the reaction mixture was then cooled to room temperature. After filtration, the solid fraction was washed with cold methanol and dried under reduced pressure. Furthermore, the obtained solid was purified by recrystallization from hexane to mainly remove residual methanol. The crystalline orange solid was filtered and then dried under reduced pressure (2.25 g, 72.7 mmol, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C): δ 13.68 (1H, s, O*H*), 8.63 (1H, s, N=C*H*), 7.46 (1H, d, *J* = 2.9 Hz, C*H*-phenol), 7.42–7.38 (2H, m, C*H*-aniline), 7.30–7.23 (3H, m, C*H*-aniline), 7.22 (1H, d, *J* = 2.4 Hz, C*H*-phenol), 1.48, 1.33 (9H each, s, C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 163.8 (N=*C*H), 158.3 (*C*-OH), 148.8 (*ipso*-aniline), 140.6, 137.0, 118.3 (*ipso*-phenol), 128.0, 126.8 (phenol), 129.3, 126.5, 121.2 (aniline), 35.1, 34.2 (*C*(CH$_3$)$_3$), 31.5, 29.5 (C(*C*H$_3$)$_3$).

N-Cyclohexyl-3,5-di-*tert*-butylsalicylideneamine (2)

A procedure similar to that described for ligand **1** but with the use of cyclohexylamine (0.50 g, 5.04 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (1.18 g, 5.03 mmol) gave a yellow solid (1.32 g, 4.18 mmol, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C): δ 14.02 (1H, s, O*H*), 8.37 (1H, s, N=C*H*), 7.36 (1H, d, *J* = 2.5 Hz, C*H*-phenol), 7.07 (1H, d, *J* = 2.5 Hz, C*H*-phenol), 2.00–1.25 (10H, m, CH_2-cyclohexane), 1.45, 1.30 (9H each, s, C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 163.3 (N=*C*H), 158.3 (*C*-OH), 139.8, 136.7, 118.0 (*ipso*-phenol), 126.5, 125.7 (phenol), 67.6, 34.4, 25.6, 24.5 (cyclohexane), 35.0, 34.1 (*C*(CH$_3$)$_3$), 31.5, 29.5 (C(*C*H$_3$)$_3$).

N-Hydroxyethyl-3,5-di-*tert*-butylsalicylideneamine (3)

A procedure similar to that described for ligand **1** but with the use of ethanolamine (0.31 g, 4.99 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (1.19 g, 5.08 mmol) gave a yellow solid (0.78 g, 2.82 mmol, 57% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C): δ 13.53 (1H, s, O*H*), 8.42 (1H, s, N=C*H*), 7.39 (1H, d, *J* = 3.0 Hz, C*H*-phenol), 7.11 (1H, d, *J* = 3.0 Hz, C*H*-phenol), 3.93 (2H, q, OCH_2), 3.75 (2H, t, NCH_2), 1.44, 1.31 (9H each, s, C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 168.1 (N=*C*H), 158.0 (*C*-OH), 140.2, 136.7, 117.8 (*ipso*-phenol), 127.1, 126.1 (phenol), 61.8 (N*C*H$_2$), 62.3 (*C*H$_2$-OH), 35.0, 34.1 (*C*(CH$_3$)$_3$), 31.5, 29.4 (C(*C*H$_3$)$_3$).

N-Methoxyethyl-3,5-di-*tert*-butylsalicylideneamine (5)

A procedure similar to that described for ligand **1** but with the use of 2-methoxyethylamine (0.38 g, 5.06 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (1.18 g, 5.02 mmol) gave a yellow solid (1.36 g, 4.66 mmol, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 13.70 (1H, s, O*H*), 8.37 (1H, s, N=C*H*), 7.37 (1H, d, *J* = 2.8 Hz, C*H*-phenol), 7.08 (1H, d, *J* = 2.4 Hz, C*H*-phenol), 3.75 (2H, t, CH_2), 3.67 (2H, t, CH_2), 3.31 (3H, s, OCH_3) 1.44, 1.30 (9H each, s, C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 167.4 (N=*C*H), 158.1 (*C*-OH), 140.0, 136.6, 117.9 (*ipso*-phenol), 126.9, 126.0 (phenol), 72.0 (O*C*H$_2$), 59.0, 59.1 (N*C*H$_2$ and O*C*H$_3$), 35.0, 34.1 (*C*(CH$_3$)$_3$), 31.5, 29.5 (C(*C*H$_3$)$_3$).

N-Tetrahydrofurfuryl-3,5-di-*tert*-butylsalicylideneamine (6)

A procedure similar to that described for ligand **1** but with the use of tetrahydrofurfurylamine (0.51 g, 5.04 mmol)

and 3,5-di-*tert*-butylsalicylaldehyde (1.18 g, 5.04 mmol) gave an oil. After filtration, the oil was dried under reduced pressure (0.84 g, 2.65 mmol, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 13.71 (1H, s, O*H*), 8.37 (1H, s, N=C*H*), 7.37 (1H, d, *J* = 2.4 Hz, C*H*-phenol), 7.09 (1H, d, *J* = 2.4 Hz, C*H*-phenol), 3.75 (1H, m, OC*H*), 3.90–3.72 (2H, m, OCH_2), 3.68 (2H, m, NCH_2) 2.11–1.70 (4H, m, CH_2-furfulyl), 1.44, 1.30 (9H each, s, C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 167.4 (N=*C*H), 158.2 (*C*-OH), 139.9, 136.6, 117.9 (*ipso*-phenol), 126.9, 126.0 (phenol), 78.2 (O*C*H), 68.4 (OCH_2), 63.6 (NCH_2), 35.0, 34.1 (*C*(CH_3)$_3$), 31.5, 29.4 (C(*C*H_3)$_3$), 29.3, 25.8 (*C*H_2-furfuryl).

***N*-Phenyl-3-methoxysalicylideneamine (8)**

A procedure similar to that described for ligand **1** but with the use of aniline (0.47 g, 5.05 mmol) and 3-methoxysalicylaldehyde (0.77 g, 5.04 mmol) gave an orange crystal (0.54 g, 2.36 mmol, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 13.66 (1H, s, O*H*), 8.63 (1H, s, N=C*H*), 7.42 (1H, m, C*H*-aryl), 7.31–7.26 (3H, m, C*H*-aryl), 7.04–6.97 (2H, m, C*H*-aryl), 6.88 (1H, t, C*H*-phenol), 3.94 (3H, s, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 162.6 (N=*C*H), 151.5 (*C*-OH), 148.6 (*ipso*-aniline), 148.2, 119.2 (*ipso*-phenol), 129.4, 121.2 (aniline), 127.0, 125.5, 103.8, 97.9 (aniline and phenol), 56.2 (O*C*H_3).

***N*-Phenyl-4-diethylaminosalicylideneamine (9)**

A procedure similar to that described for ligand **1** but with the use of aniline (0.47 g, 5.05 mmol) and 4-(diethylamino)salicylaldehyde (0.97 g, 5.03 mmol) gave an orange solid (0.99 g, 3.71 mmol, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C): δ 13.79 (1H, s, O*H*), 8.42 (1H, s, N=C*H*), 7.37 (2H, m, C*H*-aryl), 7.25–7.12 (4H, m, C*H*-aryl), 6.25 (1H, dd, *J* = 2.0, 8.5 Hz, C*H*-phenol), 6.19 (1H, d, *J* = 2.0 Hz, C*H*-phenol), 3.41 (4H, q, CH_2CH$_3$), 1.21 (6H, t, CH$_2$CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 160.5 (N=*C*H), 164.3 (*C*-OH), 148.9 (*ipso*-aniline), 151.9, 109.2 (*ipso*-phenol), 129.3, 120.8 (aniline), 133.7, 125.5, 103.8, 97.9 (aniline and phenol), 44.6 (*C*H$_2$CH$_3$), 12.7 (CH$_2$*C*H$_3$).

***N*-(4-Hydroxyphenyl)-pyridineamine**

A procedure similar to that described for ligand **1** but with the use of 4-hydroxyaniline (0.80 g, 49.9 mmol) and 2-pyridinecarboxaldehyde (1.17 g, 49.9 mmol) gave a yellow solid. (1.11 g, 29.4 mmol, 59% yield). ^{1}H NMR (500 MHz, DMSO-d_6, 30 °C): δ 9.61 (1H, s, O*H*), 8.69 (1H, m, C*H*-pyridine), 8.60 (1H, s, N=C*H*), 8.12 (1H, m, C*H*-pyridine), 7.92 (1H, m, C*H*-pyridine), 7.48 (1H, m, C*H*-pyridine), 7.30 (2H, m, C*H*-phenol), 6.83 (2H, m, C*H*-phenol).

***N*-(4-Hexadecanoxyphenyl)-pyridineamine (15)**

N-(4-Hydroxyphenyl)-pyridineamine (0.92 g, 4.63 mmol), 1-bromohexadecane (1.42 g, 4.64 mmol), KOH (0.31 g, 5.47 mmol) and NaI (about 10 mg) were mixed in DMF (20 ml). The mixture was stirred at 70 °C overnight. After solvent was evaporated, the obtained black oil was dissolved in CH_2Cl_2 and then washed several times with 0.10 M NaOH aq. and water. The organic layer was dried over magnesium sulfate. After filtration, the solvent was evaporated. The product was recrystallized from hexane (1.14 g, 2.70 mmol, 58% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C): δ 8.70 (1H, m, C*H*-pyridine), 8.63 (1H, s, N=C*H*), 8.19 (1H, m, C*H*-pyridine), 7.80 (1H, m, C*H*-pyridine), 7.36–7.30 (3H, m, C*H*-pyridine and C*H*-phenol), 6.94 (2H, m, C*H*-phenol), 3.98 (2H, t, OCH_2), 1.80 (2H, m, OCH$_2$CH_2), 1.50–1.20 (26H, m, CH_2), 0.88 (3H, t, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ

158.1 (N=*C*H), 158.6, 143.5 (*ipso*-aniline), 155.0 (*ipso*-pyridine), 149.6, 121.6, 124.7, 136.6 (pyridine), 115.1, 122.7 (aniline), 68.3 (O*C*H_2), 31.9 (OCH_2*C*H_2), 29.7, 29.6, 29.4, 29.3, 26.1 (*C*H_2), 22.7 (*C*H_2CH_3), 14.1 (CH_2*C*H_3).

***N*, *N′*-Bis-(2,6-diisopropylphenyl)-2,3-butanediimine (16)**

A procedure similar to that described for ligand **1** but with the use of diacetyl (0.41 g, 4.79 mmol) and 2,6-di-isopropylaniline (1.70 g, 9.60 mmol) gave a yellow solid (0.68 g, 1.69 mmol, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 6.20–6.07 (6H, m, C*H*-aryl), 1.73 (4H, m, C*H*(CH_3)$_2$), 1.08 (6H, s, CC*H*$_3$), 0.20 (24H, m, CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 168.2 (N=*C*H), 146.2, 135.1 (*ipso*-aniline), 123.0, 123.7 (aniline), 28.5 (*C*H(CH_3)$_2$), 23.0, 22.7 (CH(*C*H_3)$_2$), 16.6 (C*C*H_3).

***N*-(2,6-Di-methylphenyl)- 3,5-di-*tert*-butylsalicylideneamine (17)**

A procedure similar to that described for ligand **1** but with the use of 2,6-di-methylaniline (0.61 g, 5.06 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (1.18 g, 5.05 mmol) gave a yellow solid (0.36 g, 1.08 mmol, 21% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C): δ 13.43 (1H, s, O*H*), 8.33 (1H, s, N=C*H*), 7.48 (1H, d, *J* = 2.4 Hz, C*H*-phenol), 7.14 (1H, d, *J* = 2.4 Hz, C*H*-phenol), 7.08 (2H, m, C*H*-aniline), 7.00 (1H, m, C*H*-aniline), 2.21 (6H, s, Ar-C*H*$_3$), 1.49, 1.33 (9H each, s, C(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 167.7 (N=*C*H), 158.4 (*C*-OH), 148.4 (*ipso*-aniline), 140.4, 128.5, 137.2, 117.8 (*ipso*-phenol), 128.0, 126.6 (phenol), 128.3, 124.7 (aniline), 35.2, 34.2 (*C*(CH_3)$_3$), 31.5, 29.5 (C(*C*H_3)$_3$), 18.6 (Ar-*C*H_3).

***N*-(4-Methoxyphenyl)-3,5-di-*tert*-butylsalicylideneamine (18)**

A procedure similar to that described for ligand **1** but with the use of 4-methoxyaniline (0.62 g, 50.2 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (1.18 g, 50.2 mmol) gave a yellow solid (1.17 g, 34.5 mmol, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C): δ 13.82 (1H, s, O*H*), 8.61 (1H, s, N=C*H*), 7.43 (1H, d, *J* = 2.1 Hz, C*H*-phenol), 7.26 (2H, d, *J* = 8.9 Hz, C*H*-aniline), 7.20 (1H, d, *J* = 2.7 Hz, C*H*-phenol), 6.93 (2H, d, *J* = 8.9 Hz, C*H*-aniline), 3.82 (3H, s, OC*H*$_3$), 1.48, 1.33 (9H each, s, C(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 161.8 (N=*C*H), 158.1 (*C*-OH), 158.6, 141.7 (*ipso*-aniline), 140.5, 136.9, 118.5 (*ipso*-phenol), 127.5, 126.5 (phenol), 114.6, 122.2 (aniline), 55.5 (O*C*H_3), 35.1, 34.2 (*C*(CH_3)$_3$), 31.5, 29.5 (C(*C*H_3)$_3$).

***N*-(4-Trifluoromethylphenyl)-3,5-di-*tert*-butylsalicylideneamine (19)**

A procedure similar to that described for ligand **1** but with the use of 4-trifluoromethylaniline (0.80 g, 49.9 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (1.17 g, 49.9 mmol) gave a yellow solid (1.11 g, 29.4 mmol, 59% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C): δ 13.30 (1H, s, O*H*), 8.63 (1H, s, N=C*H*), 7.66 (2H, d, *J* = 8.6 Hz, C*H*-aniline), 7.50 (1H, d, *J* = 2.6 Hz, C*H*-phenol), 7.34 (2H, d, *J* = 8.3 Hz, C*H*-aniline), 7.24 (1H, d, *J* = 2.4 Hz, C*H*-phenol), 1.48, 1.34 (9H each, s, C(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 165.5 (N=*C*H), 158.4 (*C*-OH), 151.8 (*ipso*-aniline), 140.9, 137.2, 118.0 (*ipso*-phenol), 128.9, 127.2 (phenol), 128.3 (q, *J* = 32.4 Hz*, ipso*-aniline), 126.6 (q, *J* = 3.8 Hz, aniline), 121.5 (aniline), 124.2 (q, *J* = 270.3 Hz, *C*F_3) 35.1, 34.2 (*C*(CH_3)$_3$), 31.4, 29.4 (C(*C*H_3)$_3$).

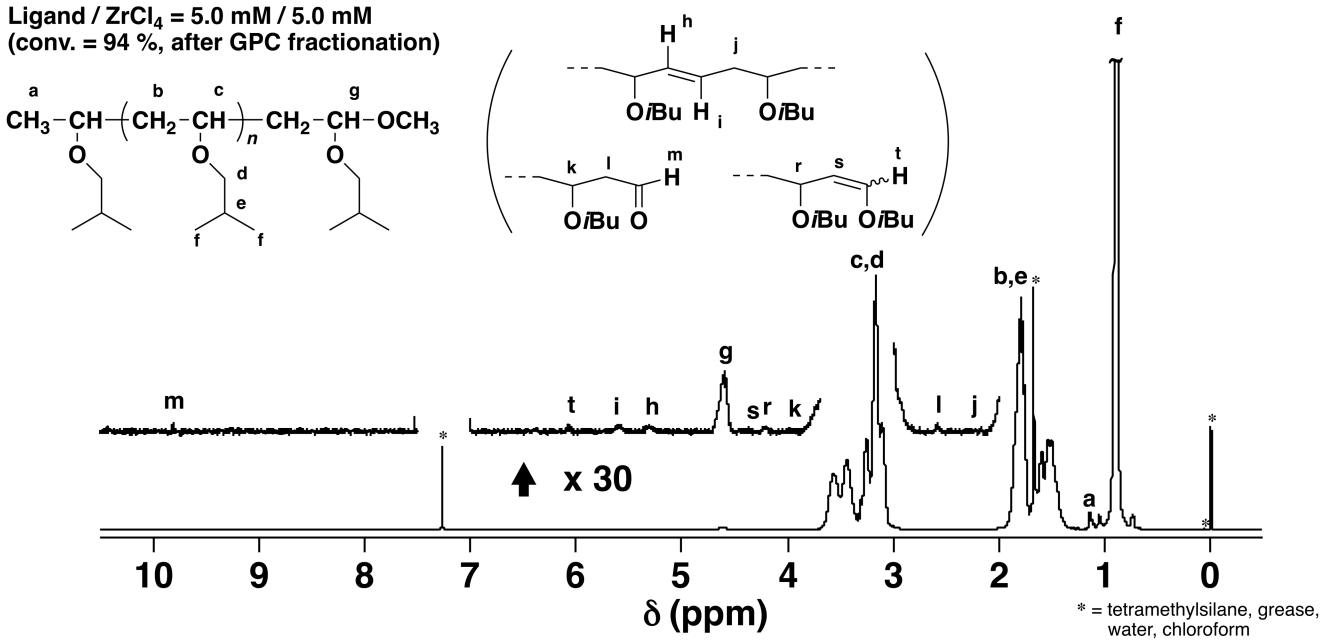

Fig. S1 ^{1}H NMR spectrum of poly(IBVE) obtained using the **1**/$ZrCl_4$ initiating system ($[IBVE]_0$ = 0.76 M, $[ZrCl_4]_0$ = 5.0 mM, $[\mathbf{1}]_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, [heptane] = 5.0 vol % in toluene at 0 ºC; 500 MHz in $CDCl_3$ at 30 ºC).

Table S1 Appearance of the catalytic solution prepared from various ligands and $ZrCl_4$.[a]

entry	coordination atoms	ligand	catalytic solution	corresponding Table or Figure
1	[*N,O*]	**1**	transparent	Fig.2, 3; Table 5, entries 1–5
2		**2**	transparent	Table 1, entry 1
3		**3**	transparent	Table 1, entry 2
4		**4**	transparent	Table 1, entry 3
5		**5**	transparent	Table 1, entry 4
6		**6**	transparent	Table 1, entry 5
7		**7**	heterogeneous	Table 1, entry 6
8		**8**	heterogeneous	Table 1, entry 7
9		**9**	heterogeneous	Table 1, entry 8
10	[*O,O*]	**10**	transparent	Table 2, entry 1
11		**11**	transparent	Table 2, entry 2
12		**12**	transparent	Table 2, entry 3
13		**13**	heterogeneous	Table 2, entry 4
14		**14**	transparent	Table 2, entry 5
15	[*N,N*]	**15**	heterogeneous	Table 2, entry 6
16		**16**	transparent	Table 2, entry 7
24	[*N,O*]	**17**	transparent	Table 5, entry 6
25		**18**	transparent	Fig. 8B
26		**19**	transparent	Fig. 8C
27	[*N,N,O,O*]	**20**	transparent	Table 5, entry 7

[a] $[ZrCl_4]_0$ = 50 mM, $[ligand]_0$ = 50 mM, [ethyl acetate] = 1.0 M, in dichloromethane at 0 °C.

Table S2 The apparent rate constants (k_{app}) of the polymerization using the various ligands and $ZrCl_4$[a]

entry	ligand	ethyl acetate (M)	k_{app} (10^{-2} h^{-1})[b]	R^2 value[b]	corresponding Table or Figure
1	**1**	1.0	1.96	0.9991	Fig.2
2	**2**	1.0	6.61	0.9994	Table 1, entry 1
3	**3**	1.0	4.68	0.9971	Table 1, entry 2
4	**4**	1.0	1.96	0.9869	Table 1, entry 3
5	**5**	1.0	1.08	0.9996	Table 1, entry 4
6	**6**	1.0	0.53	0.9924	Table 1, entry 5
7	**7**	1.0	2.04	0.8980	Table 1, entry 6
8	**8**	1.0	4.05	0.9904	Table 1, entry 7
9	**9**	1.0	0.54	0.9284	Table 1, entry 8
10	**10**	1.0	8.06	0.9974	Table 2, entry 1
11	**11**	1.0	15.0	0.9993	Table 2, entry 2
12	**12**	1.0	23.2	0.9945	Table 2, entry 3
13	**13**	0.1	37.7	0.9963	Table 2, entry 4
14	**14**	1.0	15.0	0.9993	Table 2, entry 5
15	**15**	0.1	2.72	0.9981	Table 2, entry 6
16	**16**	1.0	49.1	0.9992	Table 2, entry 7
17	No ligand	1.0	18.2	0.9996	Table 2, entry 8

[a] $[IBVE]_0$ = 0.76 M, $[ZrCl_4]_0$ = 5.0 mM, $[ligand]_0$ = 0 or 5.0 mM, [ethyl acetate] = 0.1 or 1.0 M, [heptane] = 5.0 vol% in toluene at 0 °C. [b] Calculated from $\ln([M]_0/[M])$–time plots.

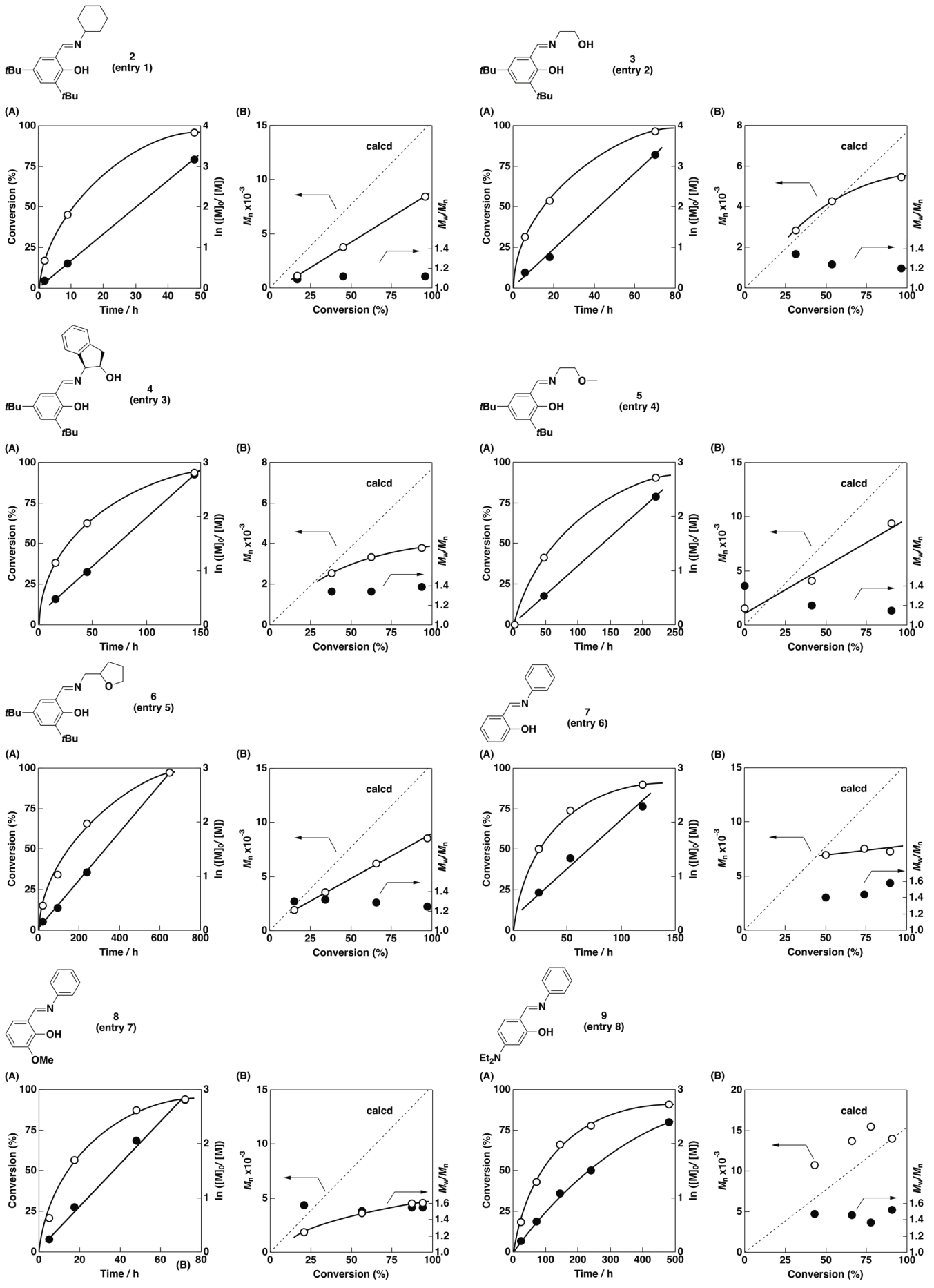

Fig. S2 (A) Time–conversion curves and ln([M]$_0$/[M])–time plots of the polymerization of IBVE using $ZrCl_4$ and various [*N*,O]-type ligands, and (B) M_n (dotted line: calculated line) and M_w/M_n values of the obtained polymers (reaction conditions: see the caption of Table 1).

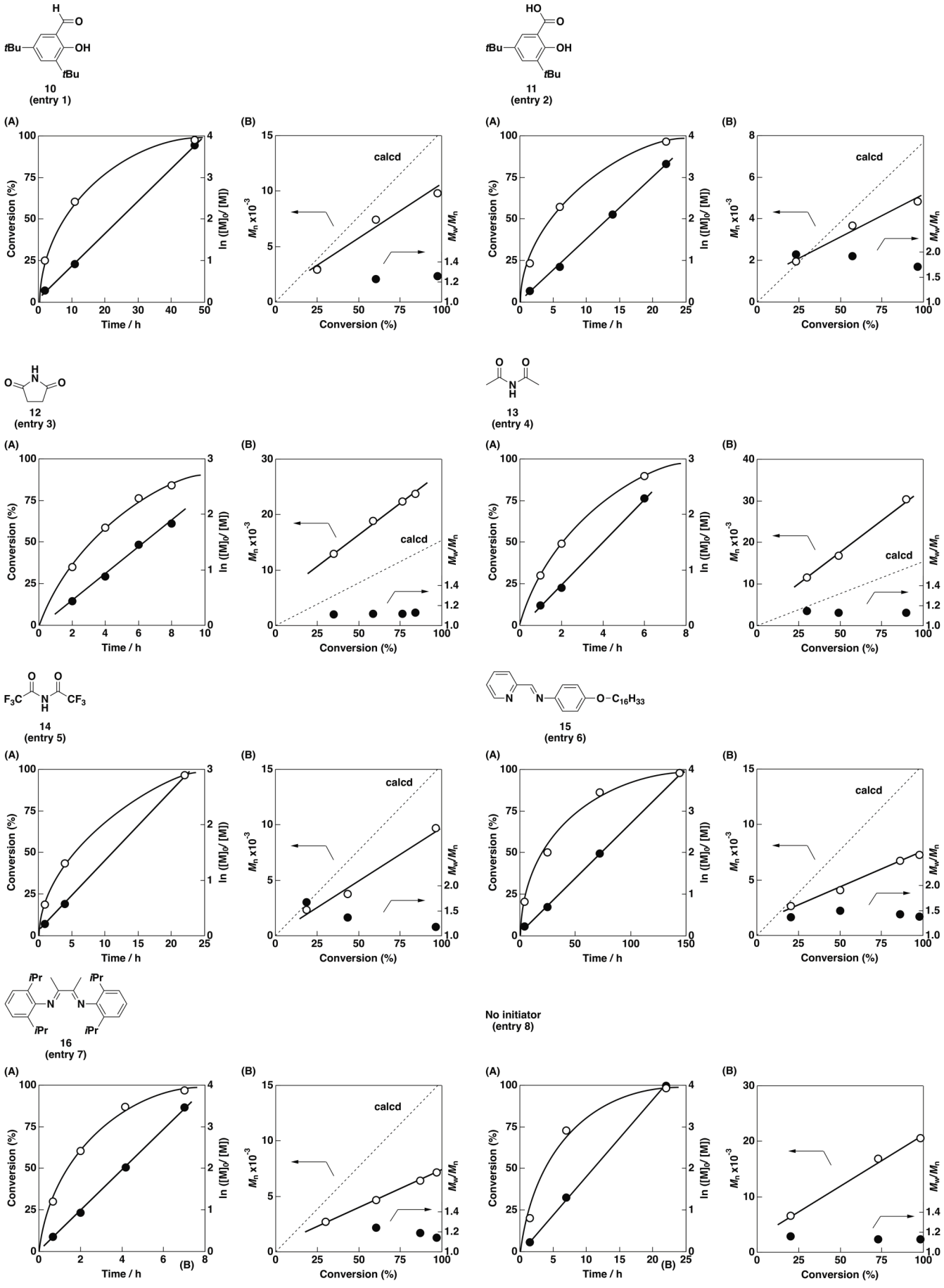

Fig. S3 (A) Time–conversion curves and ln([M]$_0$/[M])–time plots of the polymerization of IBVE using $ZrCl_4$ and various ligand frameworks, and (B) M_n (dotted line: calculated line) and M_w/M_n values of the obtained polymers (reaction conditions: see the caption of Table 2).

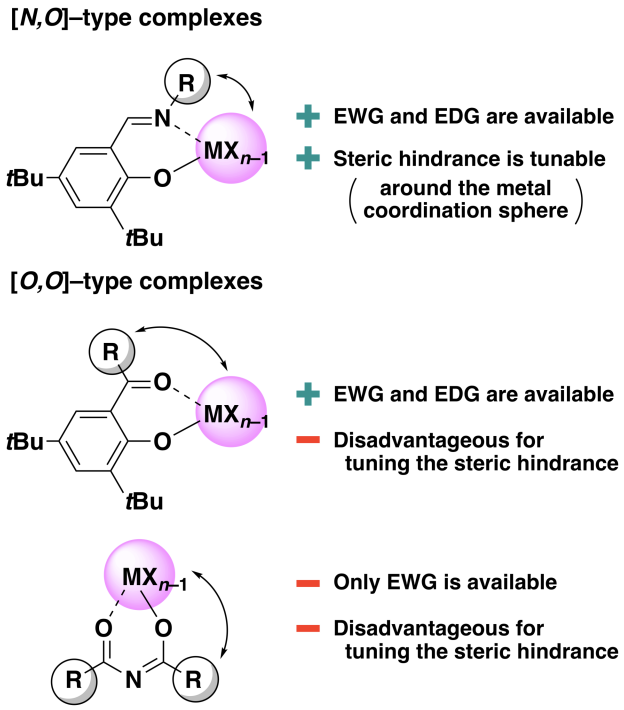

Fig. S4 The design scope of the [*N*,*O*]– and [*O*,*O*]–type complexes.

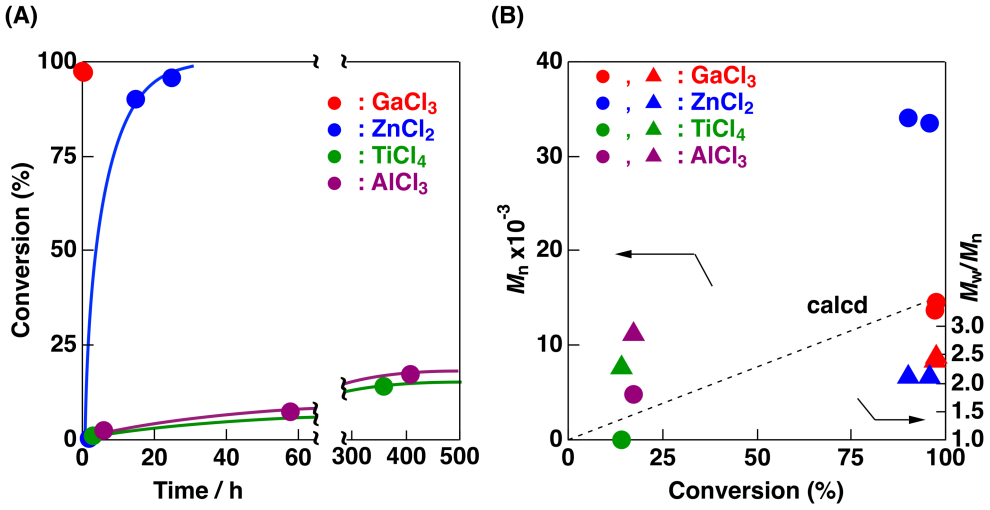

Fig. S5 (A) Time–conversion curves of the polymerization of IBVE using MCl_n and **1** and (B) M_n (dotted line: calculated line) and M_w/M_n values of the obtained polymers (reaction conditions: see the caption of Table 3).

Table S3 Appearance of the catalytic solution prepared from **1** and various metal chlorides.[a]

entry	MCl_n	ethyl acetate (M)	catalytic solution	corresponding Table or Figure number
1	$GaCl_3$	1.0	transparent	Table 3, entry 1
2		0	transparent	Table 4, entry 7
3	$ZnCl_2$	0	transparent	Table 3, entry 2; Table 4, entry 8
4	$TiCl_4$	1.0	transparent	Table 3, entries 3, 4
5		0	transparent	Table 4, entries 1, 2
6	$AlCl_3$	1.0	transparent	Table 3, entry 5
7	$ZrCl_4$	1.0	transparent	Fig.2, 3; Table 5, entries 1–5
8	$ZrCl_4$[b]	0	suspension	Table 4, entry 4
9	$HfCl_4$[b]	0	suspension	Table 4, entry 5
10	$SnCl_4$	0	slightly turbid	Table 4, entry 6

[a] $[MCl_n]_0$ = 50 mM, $[\mathbf{1}]_0$ = 50 mM, in dichloromethane and/or toluene at 0 °C. [b] Solid metal chloride was directly mixed with a ligand.

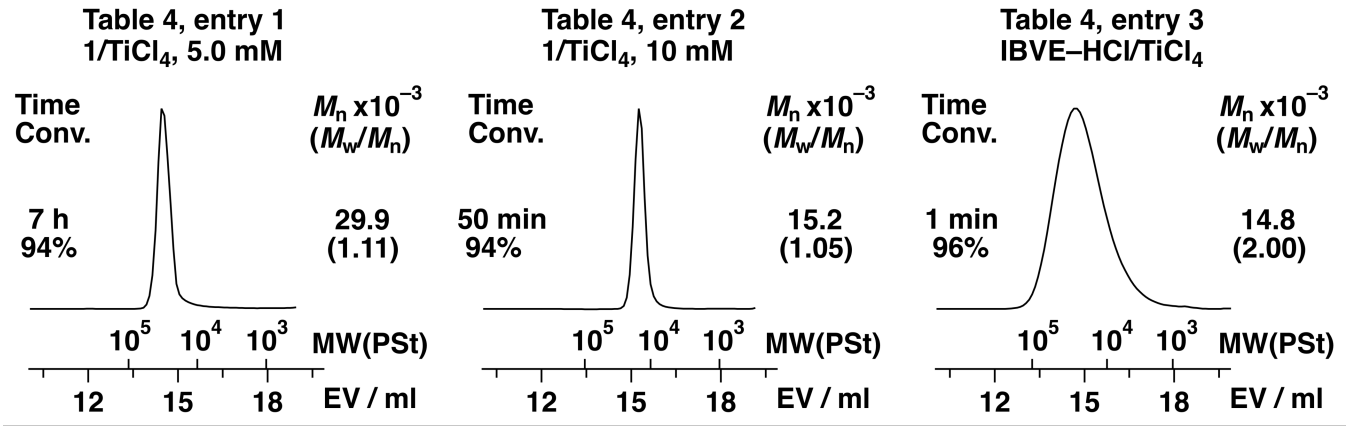

Fig. S6 MWD curves of poly(IBVE)s obtained using the **1**/$TiCl_4$ initiating system or the IBVE–HCl/$TiCl_4$ system ($[IBVE]_0$ = 0.76 M, $[\mathbf{1}]_0 = [TiCl_4]_0$ = 5.0 or 10 mM or $[IBVE–HCl]_0 = [TiCl_4]_0$ = 5.0 mM, [heptane] = 5.0 vol% in toluene at –78 °C).

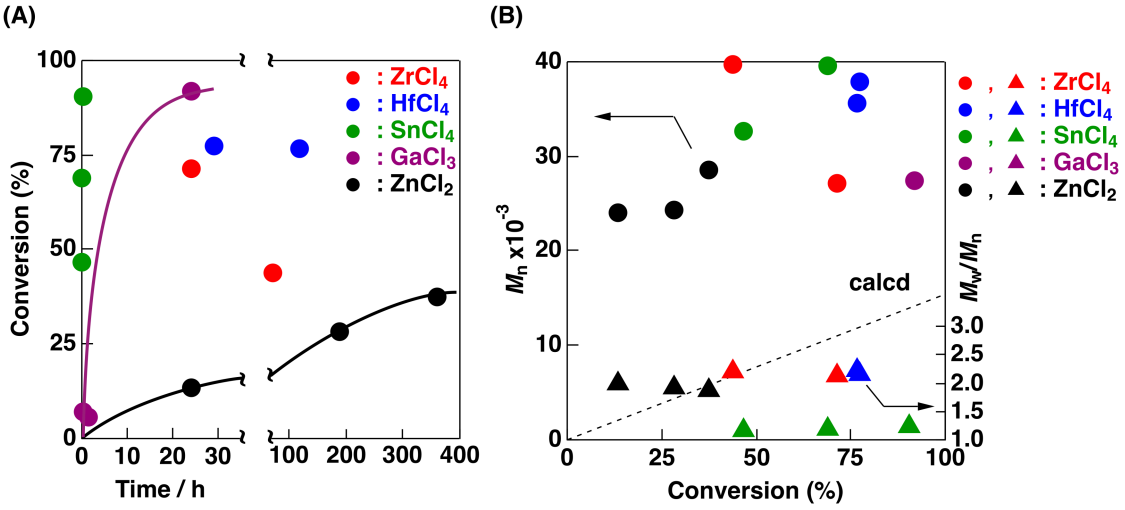

Fig. S7 (A) Time–conversion curves of the polymerization of IBVE using MCl_n and **1** in the absence of ethyl acetate and (B) M_n (dotted line: calculated line) and M_w/M_n values of the obtained polymers (reaction conditions: see the caption of Table 4).

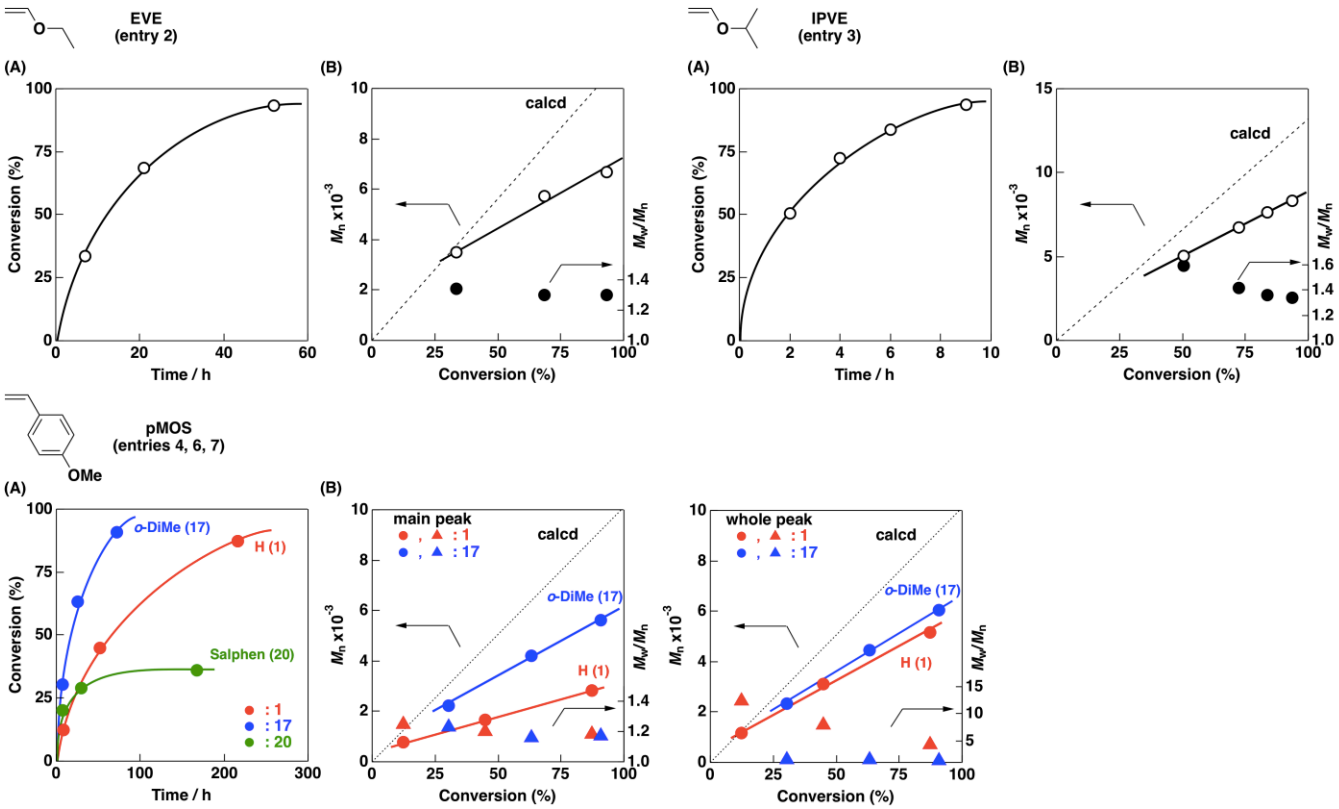

Fig. S8 (A) Time–conversion curves of the polymerization of various monomers using $ZrCl_4$ and **1**, **17**, or **20** and (B) M_n (dotted line: calculated line) and M_w/M_n values of the obtained polymers (reaction conditions: see the caption of Table 5).

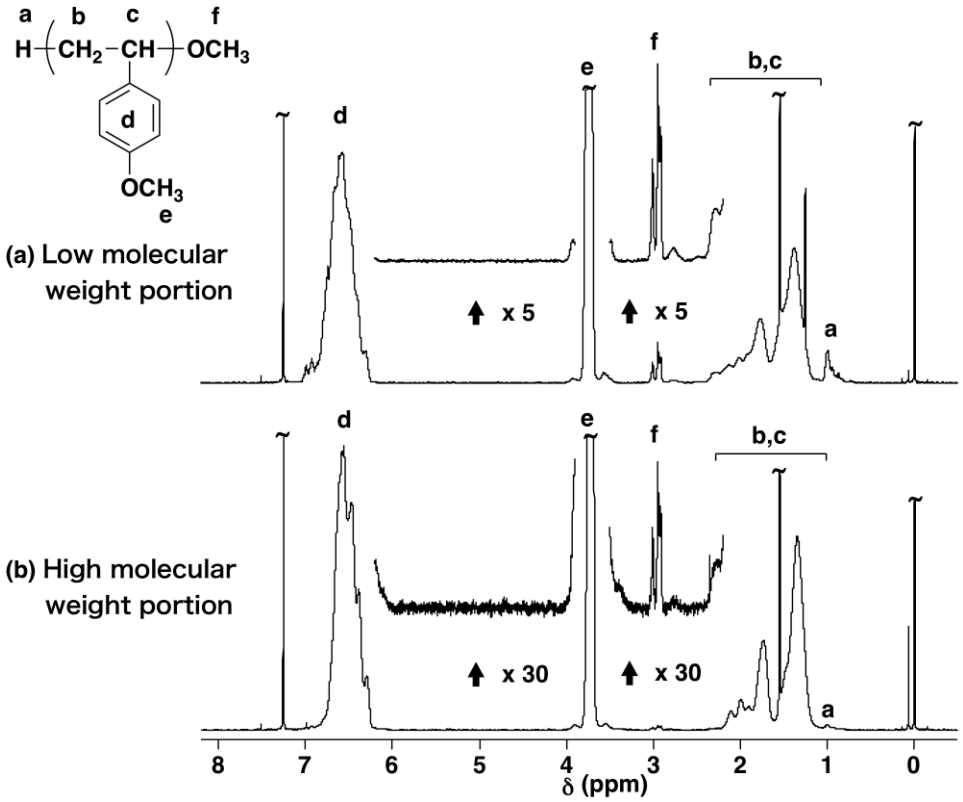

Fig. S9 ^{1}H NMR spectra of high- and low-molecular-weight portions (these portions were separated by preparative GPC) of the poly(pMOS) obtained using the **1**/$ZrCl_4$ initiating system (reaction conditions: see the caption of Table 5; 500 MHz in $CDCl_3$ at 30 ºC).

Notes: The high- and low-molecular-weight portions of the product polymers obtained using the **1**/$ZrCl_4$ initiating systems had no irregular structures originating from an undesired reaction, i.e., the *β*-proton elimination reactions (the broad peaks are observed at approximately 6.0 ppm) and/or the occurrence of intra- and/or intermolecular Friedel–Crafts reactions (the broad peaks are observed at 4.1–4.3 ppm), which was confirmed by ^{1}H NMR (Fig. S9).[S1]

References

S1. A. Kanazawa, S. Shibutani, N. Yoshinari, T. Konno, S. Kanaoka and S. Aoshima, *Macromolecules*, 2012, **45**, 7749–7757.

Table S4 Cationic copolymerization of IBVE and pMOS using the phenoxymine ligands/$ZrCl_4$ initiating systems[a]

entry	ligand	time (h)	conv (%)[b]	conv (%)[c]	$M_n \times 10^{-4}$ (calcd)[d]	$M_n \times 10^{-4}$ (obs)[e]	M_w/M_n[e]
1	**1**	48	88	15	11.0	5.8	2.24
2		480	100	87	22.0	9.0	1.63
3	**17**	7	90	9	9.9	5.6	1.76
4		79	99	74	20.8	9.2	1.42
5	**19**	20	90	26	12.6	5.5	1.75
6		120	100	84	21.7	7.7	1.42
7	C_6F_5[g]	1	87	21	11.7	8.7	1.63
8		12	100	97	23.4	13.7	1.46
9[f]	no ligand	1	91	24	12.5	8.3	1.36
10[f]		8	100	100	23.9	12.9	1.26

[a] $[IBVE]_0 = [pMOS]_0 = 0.50$ M, $[ZrCl_4]_0 = 5.0$ mM, $[ligand]_0 = 5.0$ mM, [ethyl acetate] = 0.10 M, [heptane] = 5.0 vol% in toluene at 0 °C. [b] Determined by gas chromatography. [c] Determined by ^{1}H NMR analysis. [d] Based on the amounts of ligands. [e] Determined by GPC (polystyrene standards). [f] $[IBVE–HCl]_0 = 5.0$ mM. [g] *N*-C_6F_5 substituted phenoxyimine ligand: see Fig. S10 for ligand structure).

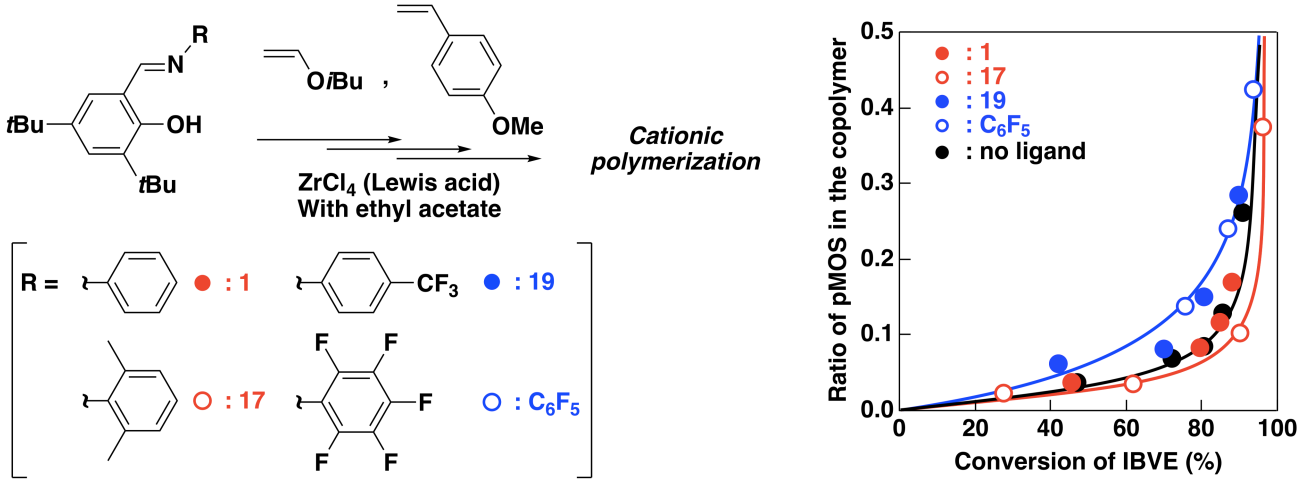

Fig. S10 The ratio of pMOS units in the products obtained in the copolymerization of IBVE and pMOS using the phenoxyimine ligands/$ZrCl_4$ initiating systems (reaction conditions: see the caption of Table S4).

Notes: Copolymerization of IBVE and pMOS proceeded successfully using the phenoxyimine/$ZrCl_4$ initiating system in a controlled, domino-type manner (Fig. S10, Table S4). The copolymerization reactions were conducted using the substituted phenoxyimines (**1**, **17**, **19**, and *N*-C_6F_5 substituted phenoxyimine ligand (C_6F_5))/$ZrCl_4$ initiating systems in the presence of ethyl acetate in toluene at 0 °C. The MWDs of the obtained polymers were monomodal but relatively broad (M_w/M_n = 1.36–1.63). The relationship between the content of pMOS in the copolymer and the conversion of IBVE is shown in Fig. S10. In all case, the pMOS contents were relatively low until the conversion of IBVE reached over 70–80%, indicating the occurrence of a domino-type reaction. The plots of **1** and **17** exhibited similar trends to those of the IBVE–HCl/$ZrCl_4$ system, which suggests that these ligands had a negligible effect on the monomer selectivity of the copolymerization. In contrast, the IBVE selectivities achieved using **19** and C_6F_5 were slightly lower than those of the above cases. The environment around the propagating carbocation and the counteranion generated from these ligands may be responsible for the decreased IBVE selectivity, although the details are unclear.

Table S5 Cationic polymerization of IBVE using various ligands/$ZrCl_4$ systems under bulk conditions[a]

entry	ligand	time	conv (%)[b]	$M_n \times 10^{-4}$ (calcd)[c]	$M_n \times 10^{-4}$ (obs)[d]	M_w/M_n[d]
1	**1**	15 h	99	15.2	6.4	1.65
2	**18**	12 h	95	14.6	7.7	1.20
3	**19**	5 min	88	13.6	3.3	4.36
4	**20**	528 h	10	0.8	0.4	8.30
5[e]	no ligand	2.5 min	74	5.1	3.0	1.92

[a] $[IBVE]_0/[complex]_0$ = 7.6 M/5.0 mM at 0 °C. [b] Determined by gas chromatography. [c] Based on the amounts of ligands. [d] Determined by GPC (polystyrene standards). [e] $[IBVE]_0$ = 6.9 M, $[IBVE–HCl]_0$ = 10 mM, $[ZrCl_4]_0$ = 5.0 mM, [ethyl acetate] = 100 mM, CH_2Cl_2: 10 vol% at 0 °C.

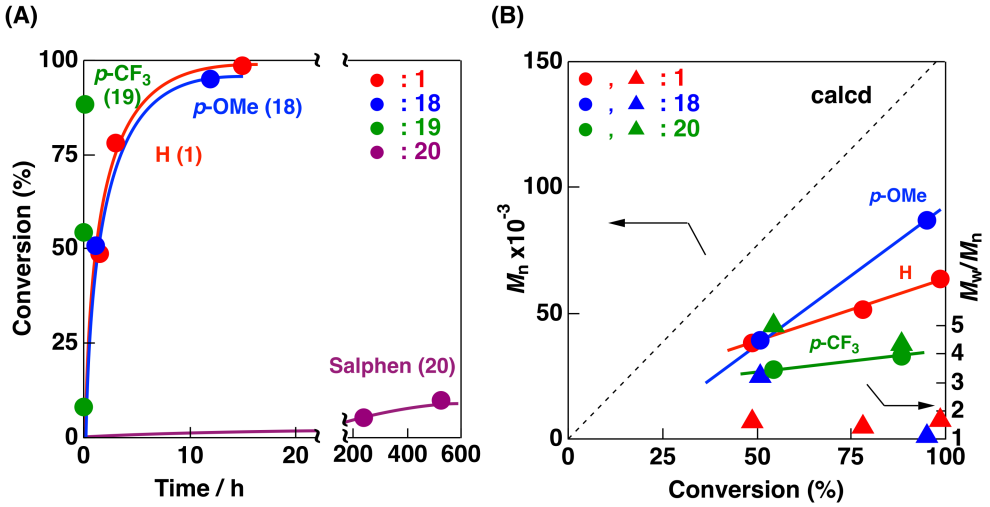

Fig. S11 (A) Time–conversion curves of the polymerization of IBVE using various ligands/$ZrCl_4$ systems under bulk conditions and (B) M_n (dotted line: calculated line) and M_w/M_n values of the obtained polymers (reaction conditions: see the caption of Table S5).