Electronic Supplementary Information for:

Frequency control of crossover reactions in concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl ethers and oxiranes: Specific roles of weak Lewis bases and solvent polarity

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Table S1. Cationic Copolymerizations of Vinyl Ethers and Oxiranes for the Determination of Monomer Reactivity Ratios [a]

Entry	VE	Oxirane	Additive	Solvent	VE conc (M)	Oxirane conc (M)	Time	Total conv (%)[b]	M_n $\times 10^{-3}$ [c]	M_w/M_n [c]	VE in copolymer [d]
1	IPVE	IBO	None	CH_2Cl_2	1.33	0.13	20 sec	3	6.9	2.72	0.94
2					1.20	0.31	40 sec	10	9.6	2.03	0.77
3					1.03	0.45	45 sec	6	5.7	2.08	0.60
4					0.95	0.52	45 sec	11	6.3	2.19	0.45
5					0.90	0.58	1 min	10	5.3	2.40	0.30
6					0.75	0.74	1 min	7	3.7	3.11	0.52
7			EtOAc	CH_2Cl_2	1.04	0.44	40 min	4	3.5	2.02	0.83
8					0.88	0.62	36 min	3	3.3	1.90	0.74
9					0.69	0.80	50 min	14	3.6	1.98	0.63
10					0.55	0.94	1 h	14	4.6	1.79	0.56
11					0.41	1.10	1.1 h	7	3.3	2.01	0.48
12			None	hex/CH_2Cl_2	1.35	0.09	1 min	1	4.7	3.82	0.92
13				(7/3 v/v)	1.20	0.30	6 min	3	3.6	2.64	0.64
14					1.02	0.43	9 min	5	3.8	2.39	0.45
15					0.89	0.59	9 min	3	2.5	2.81	0.31
16			1,4-	CH_2Cl_2	1.13	0.35	30 min	2	3.0	2.06	0.82
17			Dioxane		0.89	0.60	42 min	8	4.1	2.01	0.67
18					0.59	0.89	50 min	13	3.7	2.05	0.52
19					0.34	1.14	1 h	8	2.9	2.11	0.38
20			Et_2O	CH_2Cl_2	1.32	0.14	2 min	4	4.5	2.34	0.94
21					1.18	0.31	5 min	5	3.9	1.99	0.78
22					1.02	0.42	5 min	4	3.5	1.91	0.65
23					0.90	0.53	10 min	6	3.4	2.04	0.51
24	EVE	IBO	None	CH_2Cl_2	1.35	0.16	1 min	~0	0.5	1.41	0.44
25					1.25	0.24	3 min	1	0.6	1.53	0.35
26					1.00	0.51	5 min	1	0.7	1.70	0.18
27					0.85	0.64	5 min	1	0.6	1.67	0.12
28			EtOAc	CH_2Cl_2	1.19	0.28	3 h	4	1.1	3.34	0.64
29					0.85	0.60	5 h	9	1.1	2.08	0.45
30					0.58	0.88	5.5 h	14	1.1	1.89	0.33
31					0.31	1.02	5.5 h	14	0.8	1.81	0.24
32	IPVE	BDO	None	CH_2Cl_2	0.80	0.20	3 min	6	3.6	3.12	0.92
33					0.66	0.35	4 min	4	2.3	3.30	0.82
34					0.35	0.65	10 min	2	0.9	2.83	0.44
35					0.17	0.84	10 min	2	0.8	2.44	0.18
36			EtOAc	CH_2Cl_2	0.69	0.28	40 min	4	1.8	1.71	0.87
37					0.48	0.49	48 min	2	1.0	1.60	0.73
38					0.34	0.64	1 h	2	0.8	1.47	0.59
39					0.16	0.83	1.5 h	1	0.6	1.44	0.40
40			None	hex/CH_2Cl_2	0.79	0.19	10 min	2	1.2	3.24	0.74
41				(7/3 v/v)	0.60	0.39	30 min	4	1.0	3.15	0.51
42					0.38	0.59	40 min	3	0.9	2.59	0.26
43					0.20	0.77	1 h	2	0.9	2.69	0.13

(*Continued on next page)*

Table 1. (*Continued*)

Entry	VE	Oxirane	Additive	Solvent	VE conc (M)	Oxirane conc (M)	Time	Total conv (%)[b]	M_n $\times 10^{-3}$ [c]	M_w/M_n [c]	VE in copolymer [d]
44	IPVE	ISPO	None	CH_2Cl_2	0.85	0.16	30 min	3	1.7	2.52	0.68
45					0.75	0.22	30 min	5	2.0	3.11	0.61
46					0.64	0.35	30 min	3	1.6	2.67	0.52
47					0.35	0.65	30 min	3	1.3	2.55	0.33
48					0.17	0.86	30 min	2	1.0	2.39	0.24
49			EtOAc	CH_2Cl_2	0.83	0.12	3 h	7	2.1	2.69	0.71
50					0.62	0.34	4 h	6	1.4	2.60	0.51
51					0.37	0.58	6 h	7	1.1	2.64	0.37
52					0.21	0.79	6 h	8	0.9	2.45	0.28
53			None	hex/CH_2Cl_2	0.84	0.13	1.5 h	8	2.0	3.54	0.71
54				(7/3 v/v)	0.65	0.34	1.5 h	7	1.6	3.80	0.49
55					0.39	0.57	3 h	9	1.1	3.50	0.36
56					0.21	0.79	3 h	12	0.9	3.25	0.23

[a] $[B(C_6F_5)_3]_0$ = 1.0 (entries 1—27, 32—56) or 3.0 (entries 28—31) mM, [additive] = 0 or 1.0 M, at –78 ºC. [b] By gravimetry. [c] By GPC (polystyrene calibration). [d] By ^{1}H NMR.

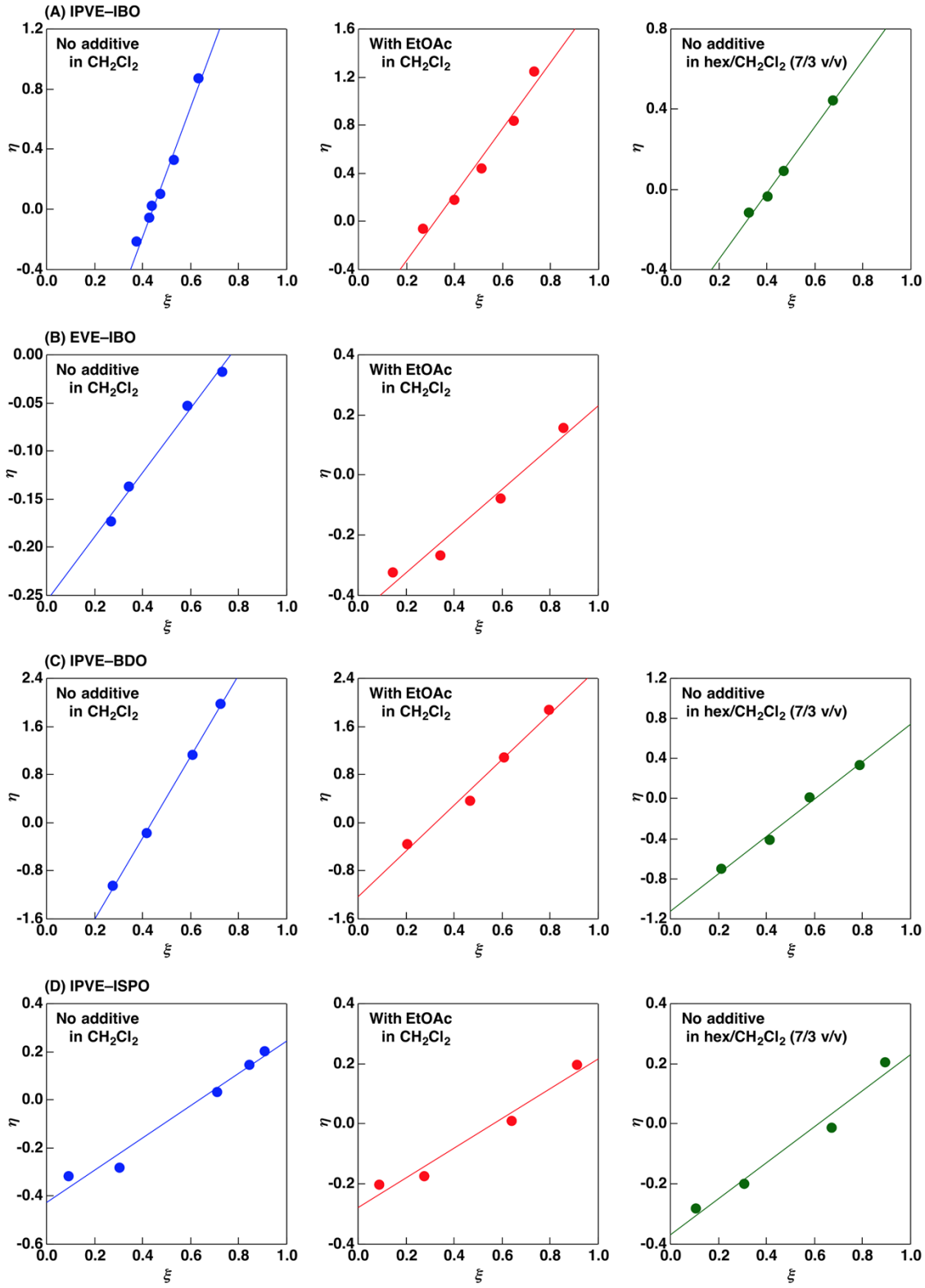

Figure S1. The plots for the determination of the monomer reactivity ratios by the Kelen–Tüdõs method [$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$; the copolymerization results listed in Table S1 were used for the calculation; see Table 2 for the monomer reactivity ratios].

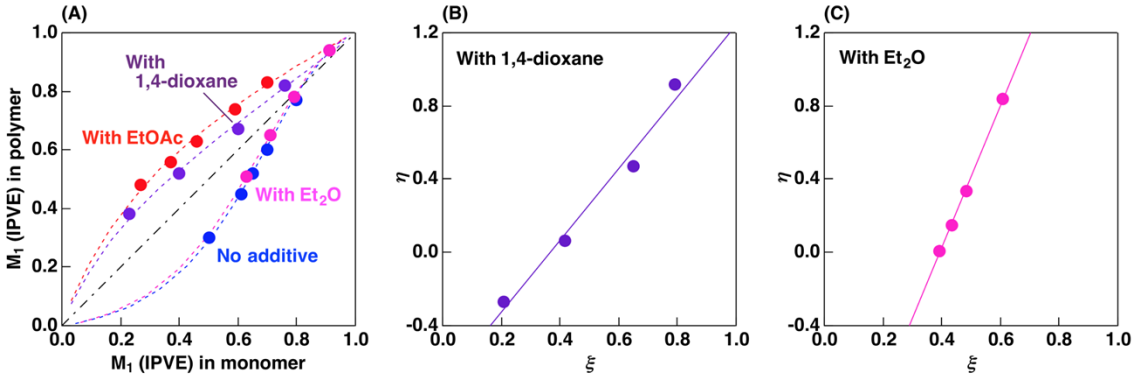

Figure S2. (A) Copolymer compositions for the cationic copolymerizations of IPVE and oxiranes and (B) and (C) the plots for the determination of the monomer reactivity ratios by the Kelen–Tüdõs method [$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$; the copolymerization results listed in Table S1 were used for the calculation; see Table 2 for the monomer reactivity ratios].

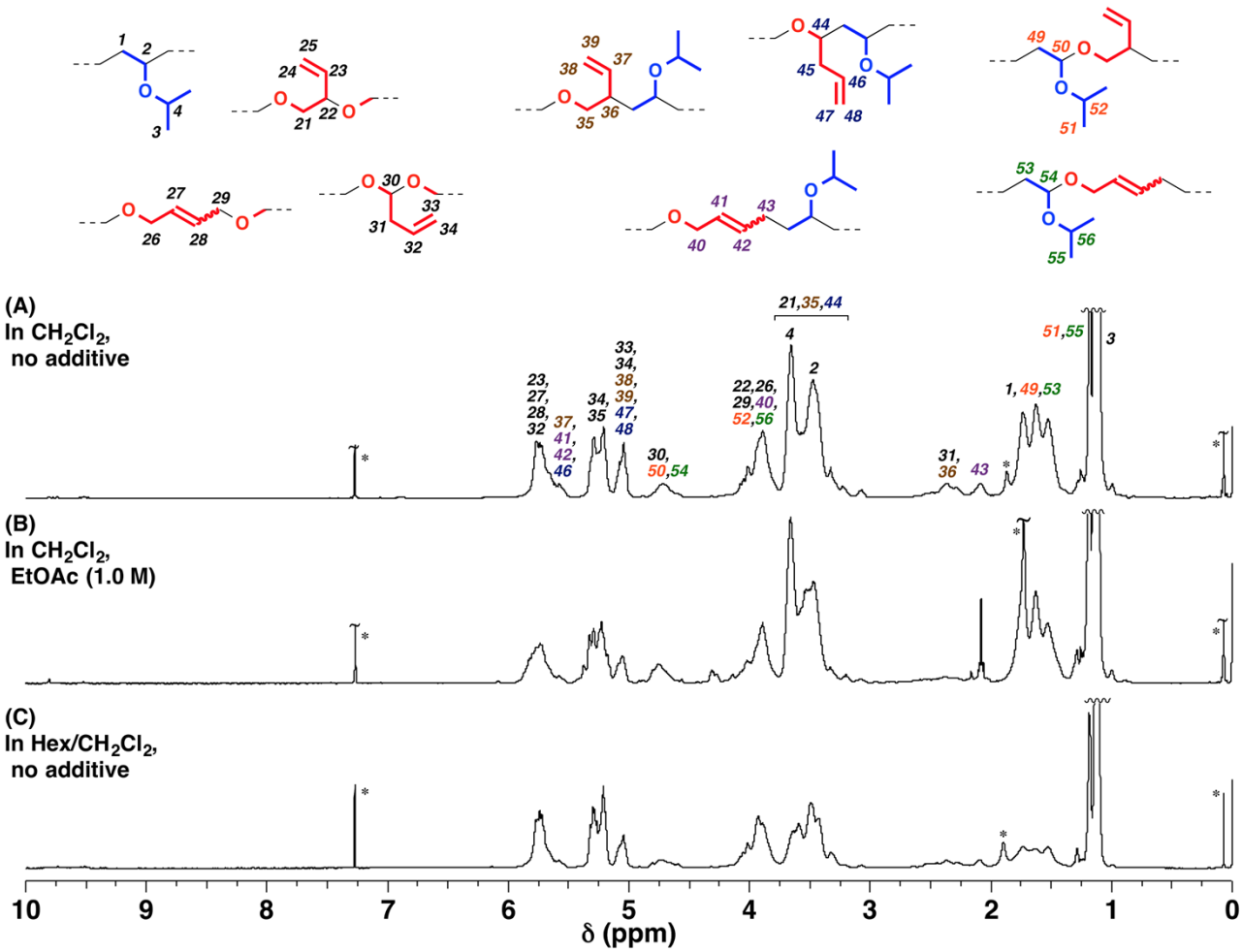

Figure S3. ^{1}H NMR spectra of the copolymerization products of IPVE and BDO: (A) entry 10, (B) entry 11, and (C) entry 12 in Table 1.

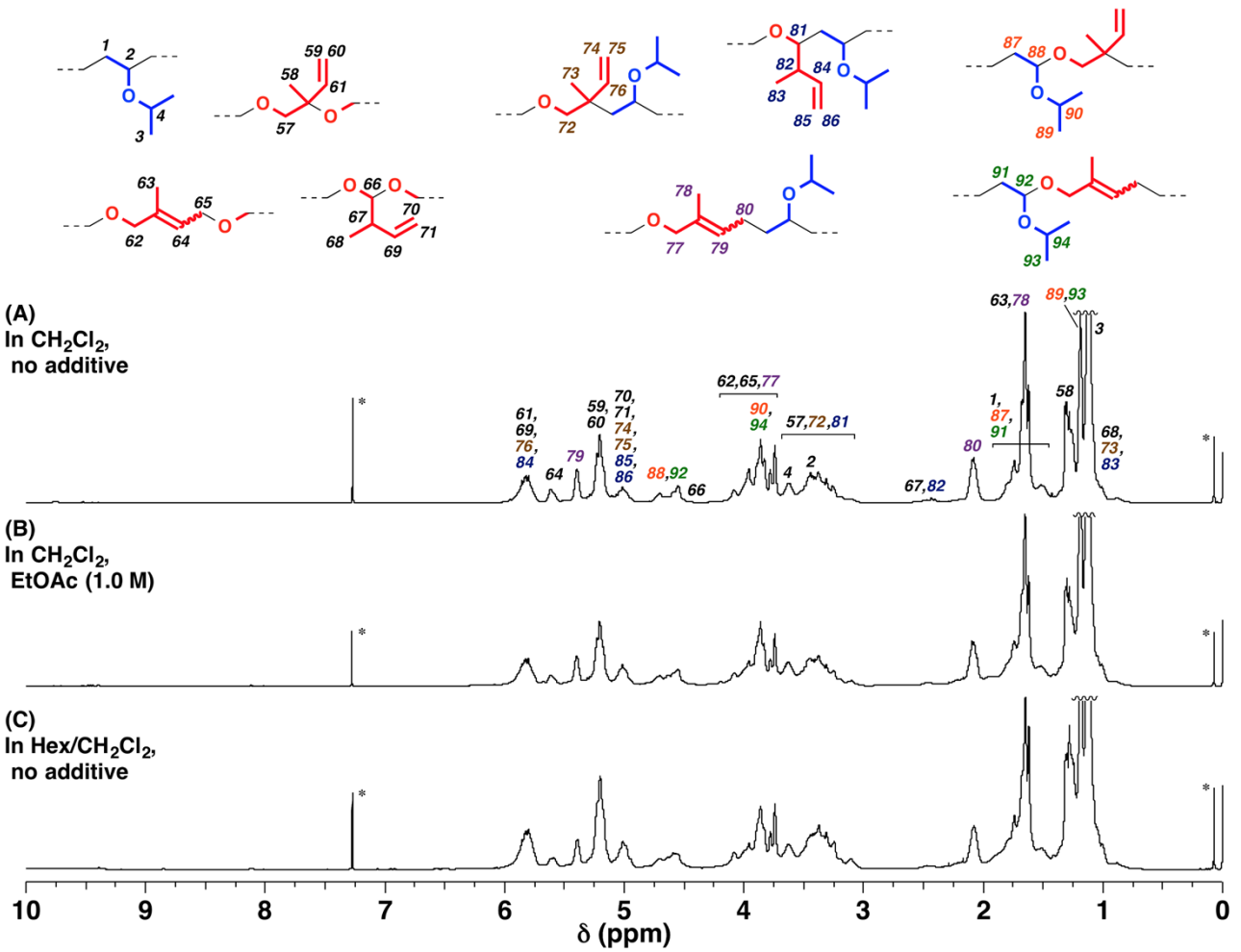

Figure S4. ^{1}H NMR spectra of the copolymerization products of IPVE and ISPO: (A) entry 13, (B) entry 14, and (C) entry 15 in Table 1.