Supporting Information

One-shot controlled/living copolymerization for various comonomer sequence distributions via dual radical and cationic active species from RAFT terminals

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Contents:

Table S1. RAFT Radical Copolymerization of Isobutyl Vinyl Ether (IBVE: M_1) and Various Acrylates (M_2) with CPETC in the Presence of $EtAl(ODBP)_2$[a]

M_2	$[IBVE]_0/[M_2]_0$	$EtAl(ODBP)_2$ (mM)	Time (h)	Conv. (%)[b] (IBVE/M_2)	M_n[c]	M_w/M_n[c]	IBVE/M_2 in copolymer[b]
MA	1500/1500	0	156	34/95	10,900	1.29	25/75
		200	6	73/99	10,200	1.75	43/57
		400	5	81/99	8,300	1.80	45/55
		600	3	83/99	7,600	2.00	46/54
MA	4500/1500	0	144	16/92	12,700	1.31	36/64
		200	5	31/99	14,300	1.42	47/53
MA	5000/1000	0	202	12/94	8,800	1.31	40/60
		200	3	19/96	10,100	1.59	48/52
MA	5400/600	0	144	6/94	5,500	1.37	43/57
		200	1.5	11/95	6,400	1.56	50/50
*n*BA	1500/1500	0	96	38/92	12,200	1.24	22/78
		200	24	63/98	9,300	1.69	43/57
*t*BA	1500/1500	0	98	34/94	12,500	1.36	19/81
		200	53	37/85	3,000	1.83	28/72

[a]Polymerization conditions: $[CPETC]_0/[V\text{-}70]_0/[EtAl(ODBP)_2]_0$ = 20/5/0 or 200 mM in toluene at 20 °C. [b]The monomer conversion and monomer composition ratio were determined by ^1H NMR. [c]The number-average molecular weight (M_n) and dispersity (M_w/M_n) were determined by size-exclusion chromatography in THF [poly(methyl methacrylate) standard].

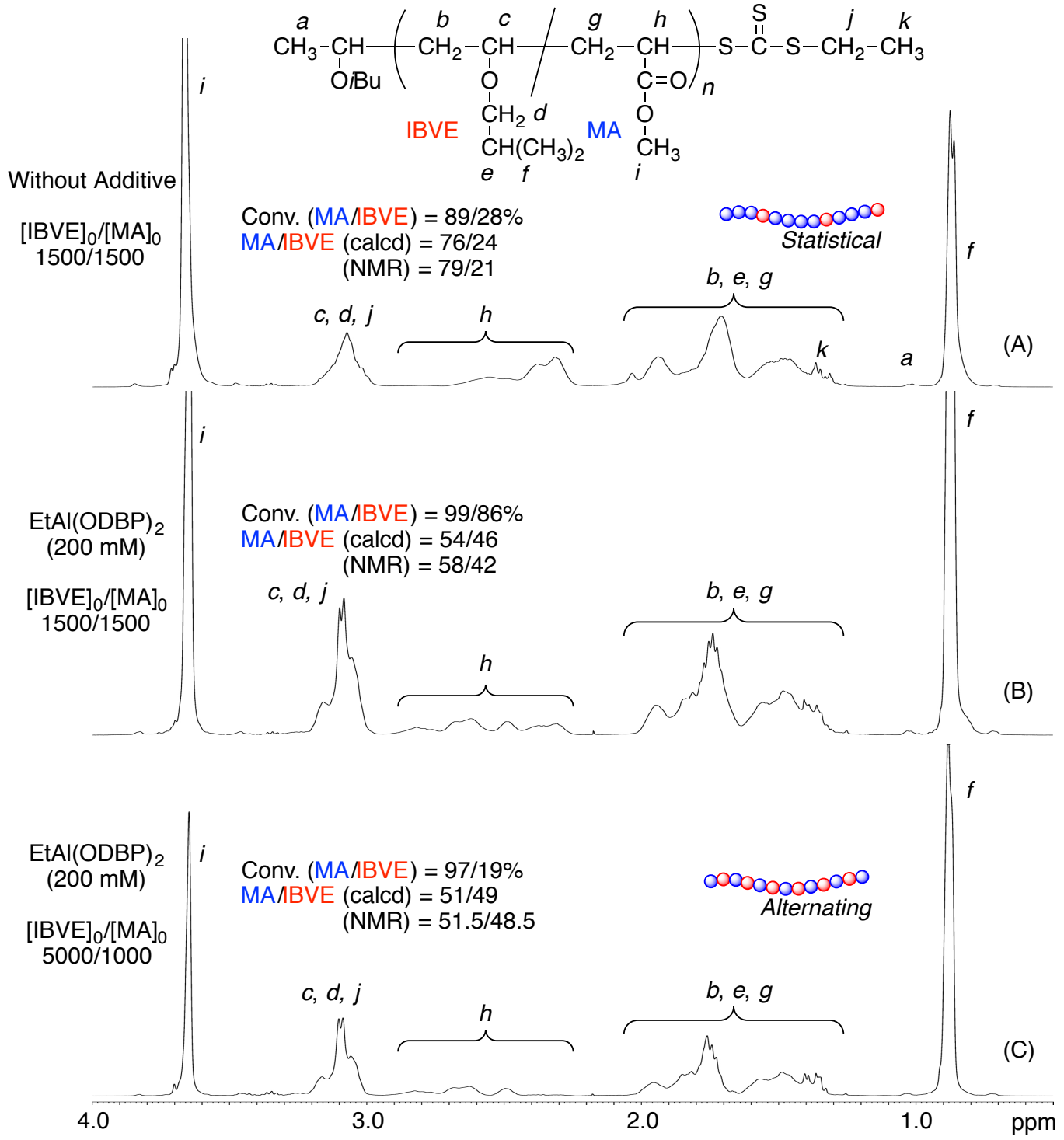

Fig. S1. ^{1}H NMR spectra of the IBVE/MA copolymers obtained with BEETC/V-70/EtAl(ODBP)$_2$ in toluene at 20 °C: $[MA]_0$ = 1.5 M and $[IBVE]_0$ = 1.5 M (for A and B); $[MA]_0$ = 1.0 M and $[IBVE]_0$ = 5.0 M (for C); $[BEETC]_0$ = 20 mM; $[V\text{-}70]_0$ = 5.0 mM; $[EtAl(ODBP)_2]_0$ = 0 (for A) or 200 mM (for B and C).

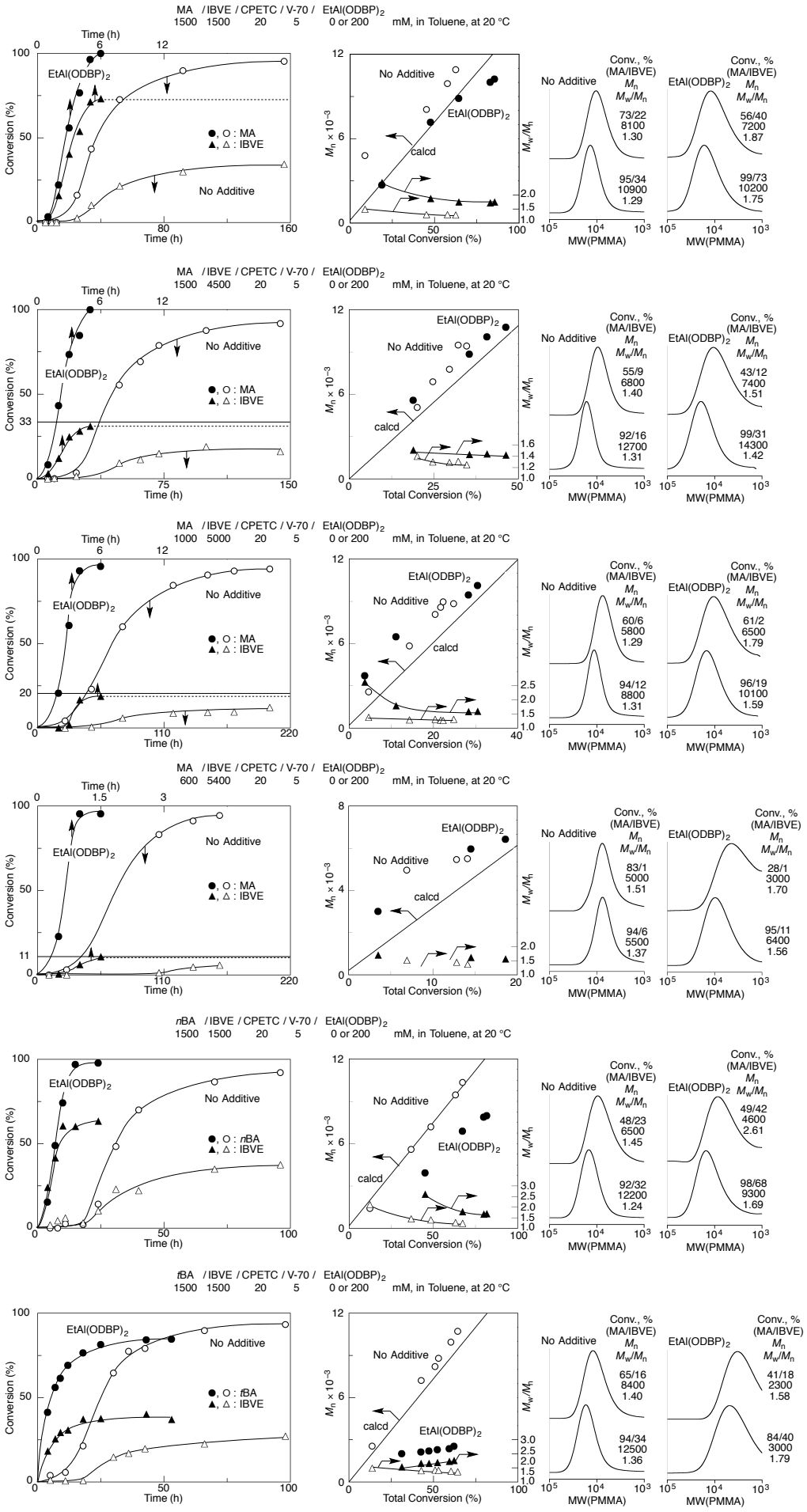

Fig. S2. RAFT radical copolymerizations of IBVE and various acrylates with CPETC/EtAl(ODBP)$_2$ shown in Table S1.

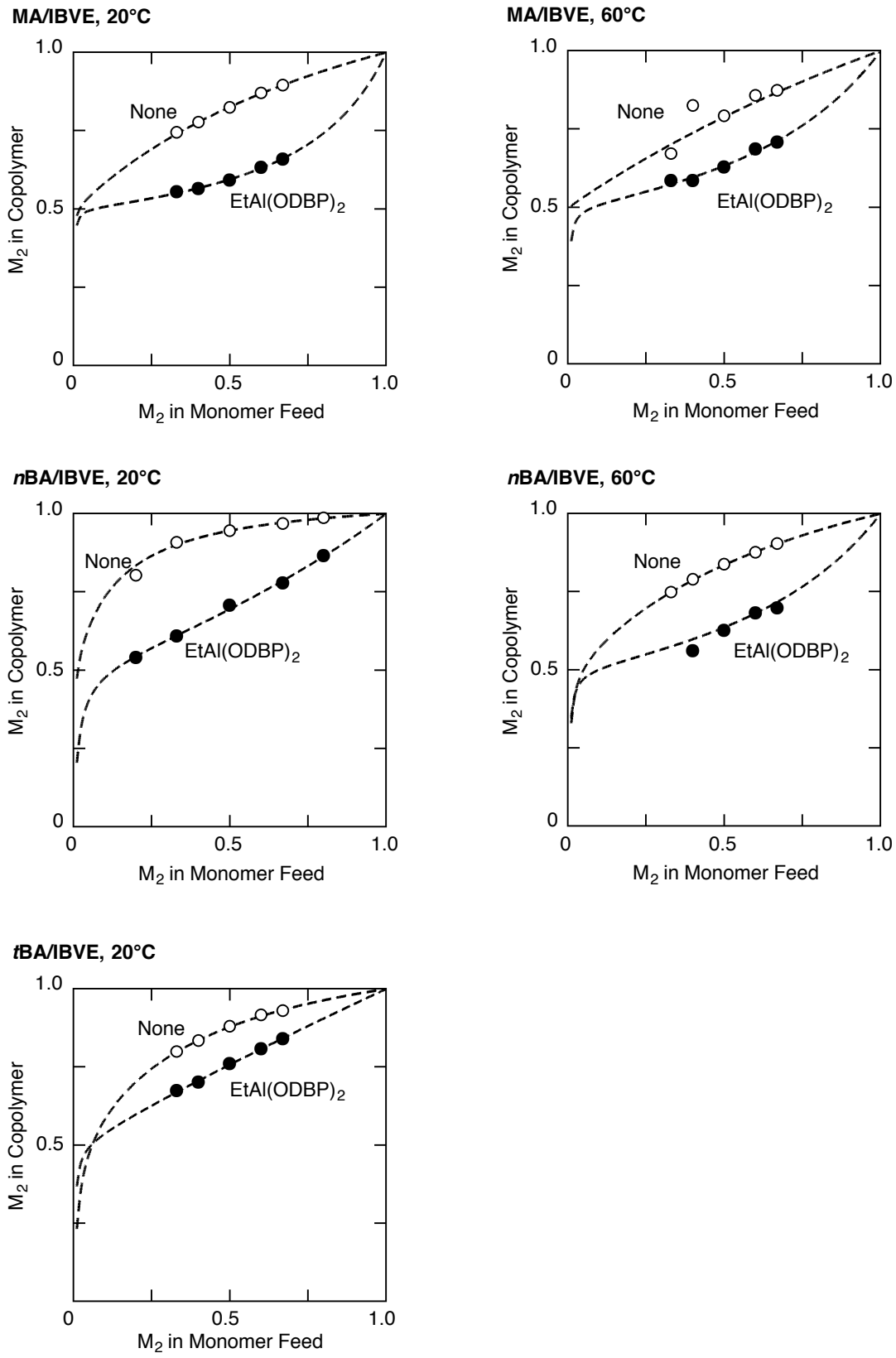

Fig. S3. Copolymer composition curves for the free radical copolymerizations of IBVE (M_1) with various acrylates (M_2) and in the presence or absence of EtAl(ODBP)$_2$: $[M_{total}]_0$ = 3.0 M, $[V\text{-}70]_0$ = 20 mM (for 20°C), $[AIBN]_0$ = 20 mM (for 60°C), $[EtAl(ODBP)_2]_0$ = 0 or 200 mM in toluene at 20 or 60 °C. Each copolymer was evaluated at low monomer conversion (<10%).

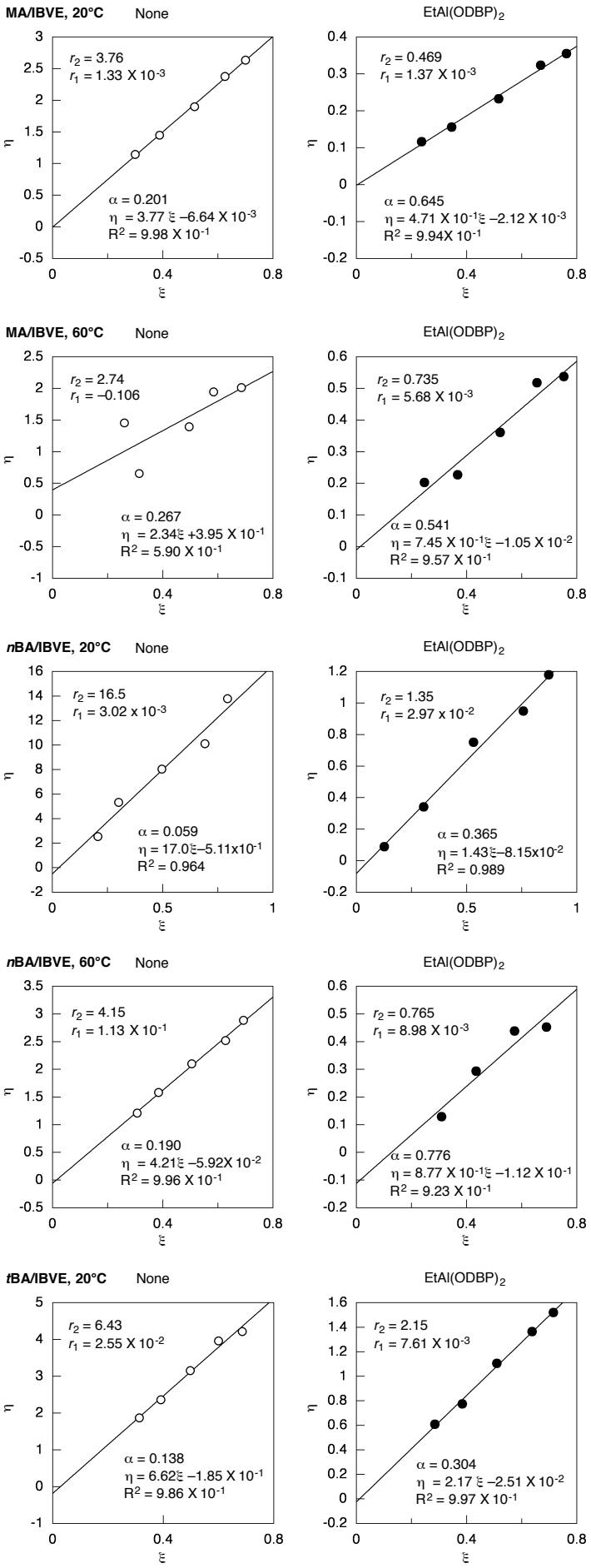

Fig. S4. Kelen–Tüdõs plots for determining the monomer reactivity ratio of IBVE (M_1) and various acrylates (M_2) and in the presence or absence of $EtAl(ODBP)_2$.

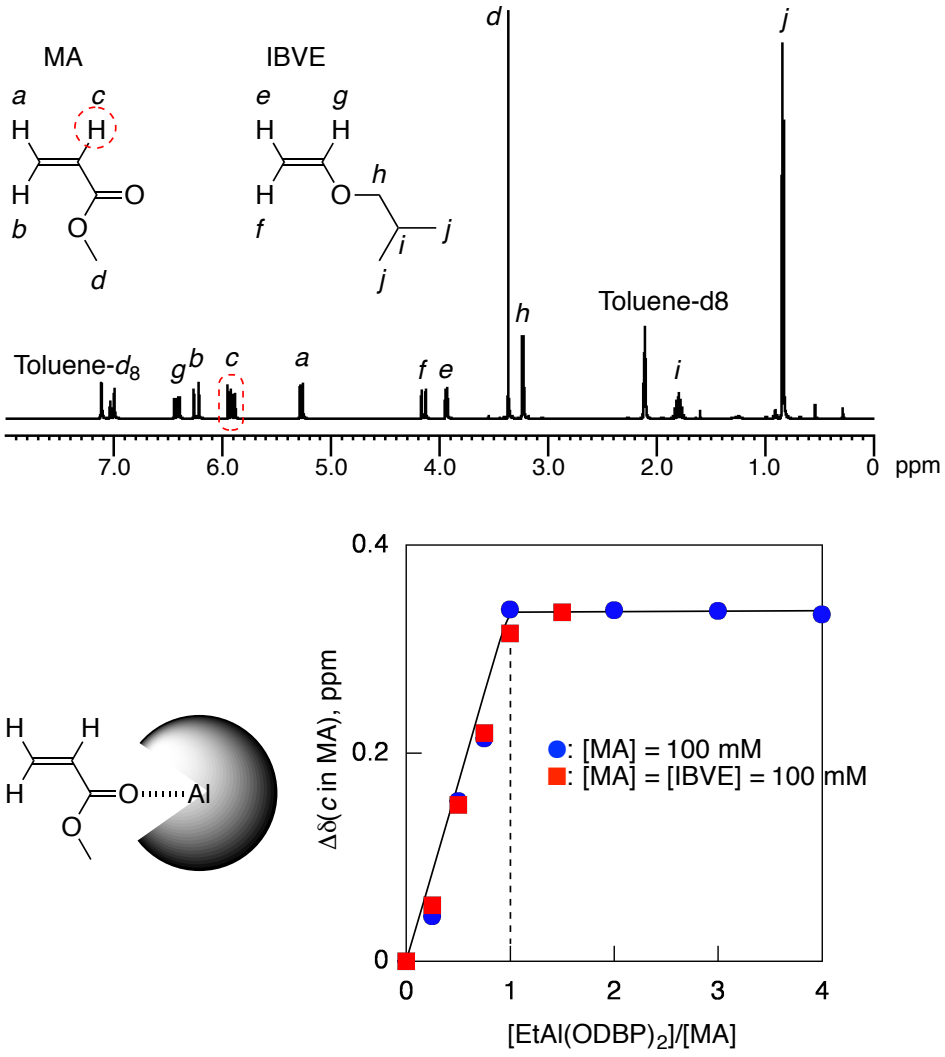

Fig. S5. Interaction between MA and EtAl(ODBP)$_2$ observed in the ^{1}H NMR spectra (toluene-d_8, 25 °C) from the changes in the acryloyl proton (*c*) chemical shifts in the presence or absence of IBVE: $[MA]_0$ = 100 mM, $[IBVE]_0$ = 0 or 100 mM, $[EtAl(ODBP)_2]_0$ = 0–400 mM.

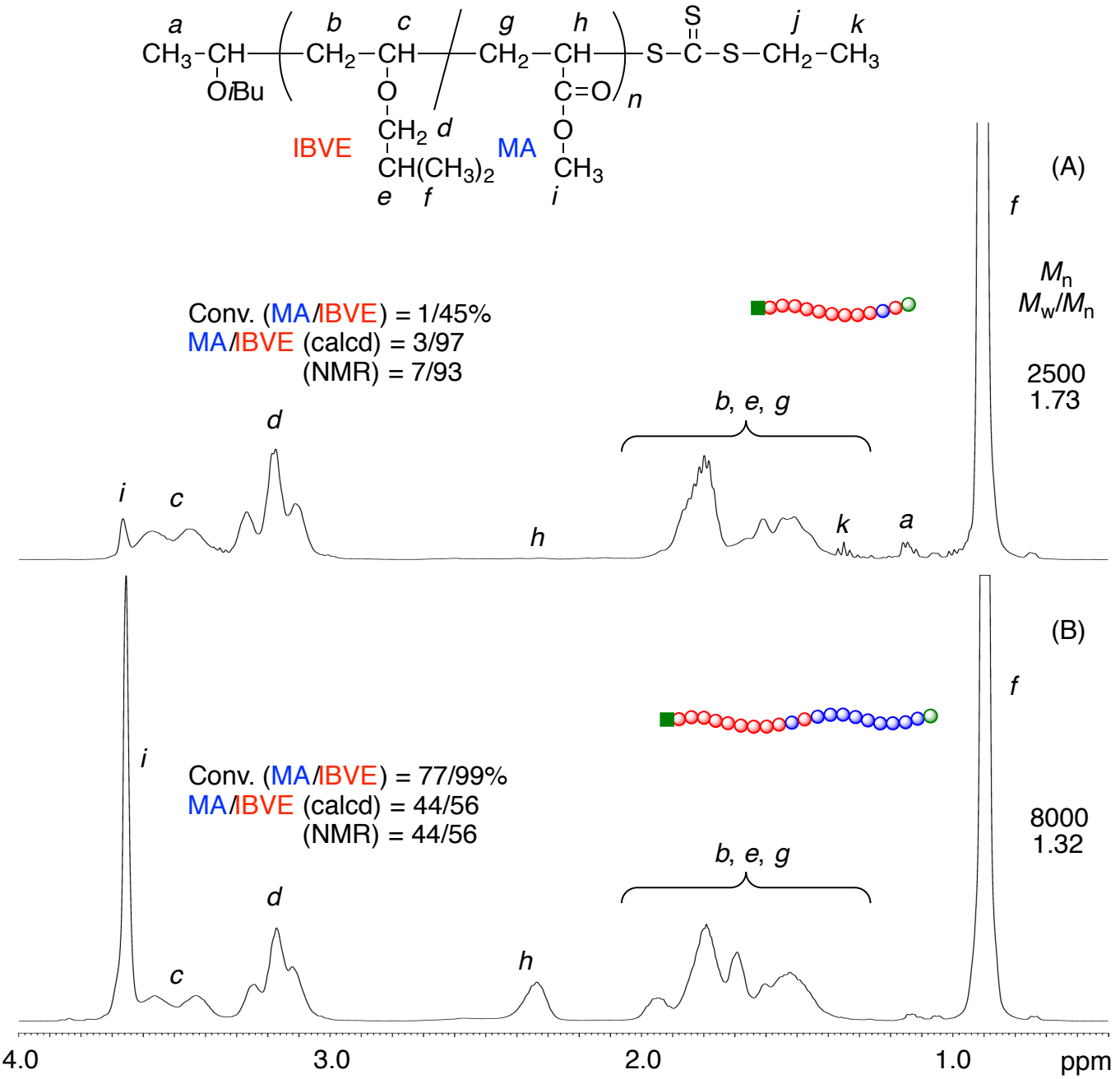

Fig. S6. ^{1}H NMR spectra ($CDCl_3$) of the one-shot kinetic block copolymers of IBVE and MA obtained with BEETC/V-70/$EtAlCl_2$ in toluene (including 9.8 vol% ethyl acetate) at 20 °C: $[MA]_0$ = 2.0 M; $[IBVE]_0$ = 2.0 M; $[BEETC]_0$ = 40 mM; $[V\text{-}70]_0$ = 10 mM; $[EtAl(ODBP)_2]_0$ = 7.5 mM. The monomer conversions were 1%/45% (A) and 77%/99% (B) for MA/IBVE, respectively.

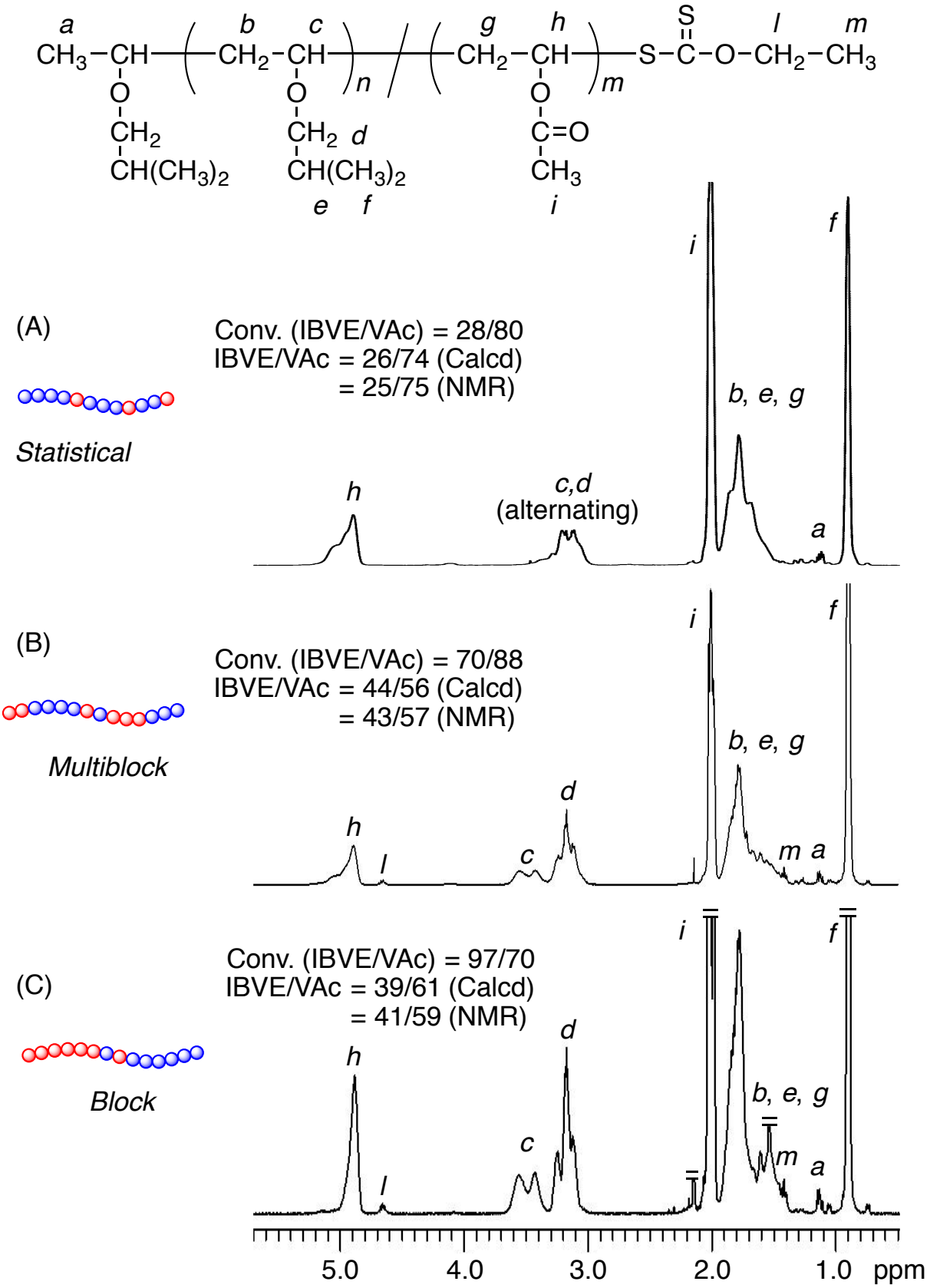

Fig. S7. ^{1}H NMR spectra ($CDCl_3$) of the VAc/IBVE copolymers obtained with BEEX/V-70/$ZnCl_2$ in ethyl acetate at 20 °C: $[VAc]_0$ = 3.0 M and $[IBVE]_0$ = 3.0 M (for A and B); $[VAc]_0$ = 4.0 M and $[IBVE]_0$ = 2.0 M (for C); $[BEEX]_0$ = 60 mM; $[V\text{-}70]_0$ = 60 (for A and B) or 30 (for C) mM; $[ZnCl_2]_0$ = 0 (for A), 1.25 (for B) or 5.0 mM (for C).