Electronic Supplementary Information for:

Controlled Cationic Copolymerization of Vinyl Monomers and Cyclic Acetals via Concurrent Vinyl-Addition and Ring-Opening Mechanisms: The Systematic Study of Structural Effects on the Copolymerization Behavior

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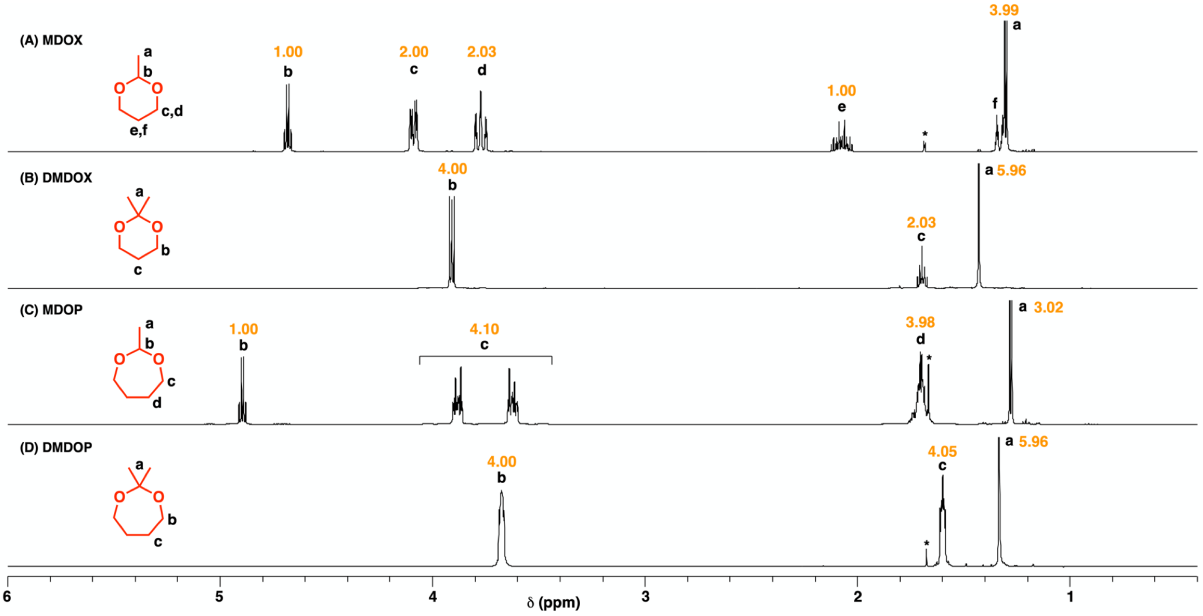


Fig. S1 ^{1}H NMR spectra of (A) MDOX, (B) DMDOX, (C) MDOP, and (D) DMDOP (in $CDCl_3$ at 30 ºC; * water; number written in orange: integral ratio).

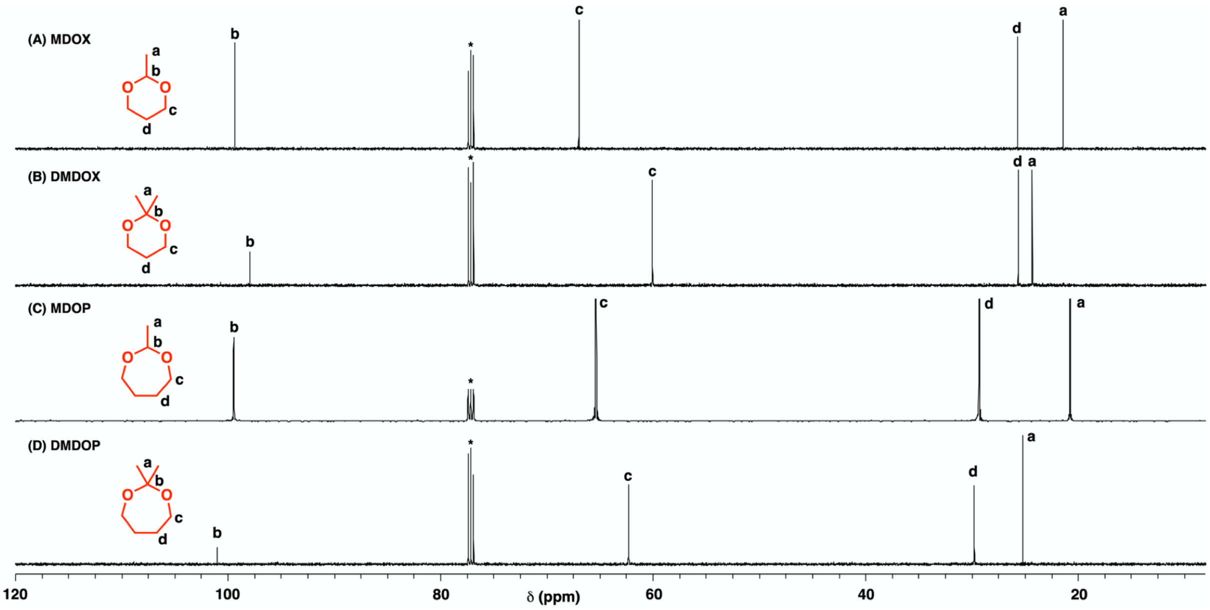


Fig. S2 ^{13}C NMR spectra of (A) MDOX, (B) DMDOX, (C) MDOP, and (D) DMDOP (in $CDCl_3$ at 30 ºC; * $CDCl_3$).

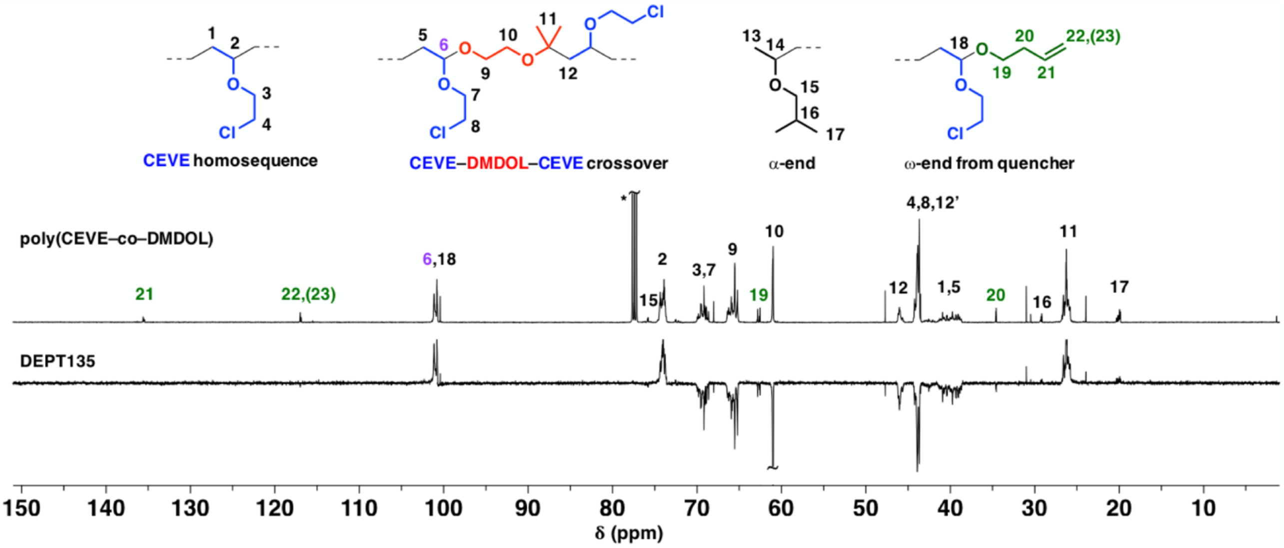


Fig. S3 ^{13}C and DEPT 135 NMR spectra of poly(CEVE-*co*-DMDOL) (entry 5 in Table 1) (in CDCl$_3$ at 30 °C; * CDCl$_3$, etc; see the caption of Fig. S6 for peak 12'; the peak of the quaternary carbon of the DMDOL-derived unit may overlap with peak 2 [see also the caption of Fig. S6]).

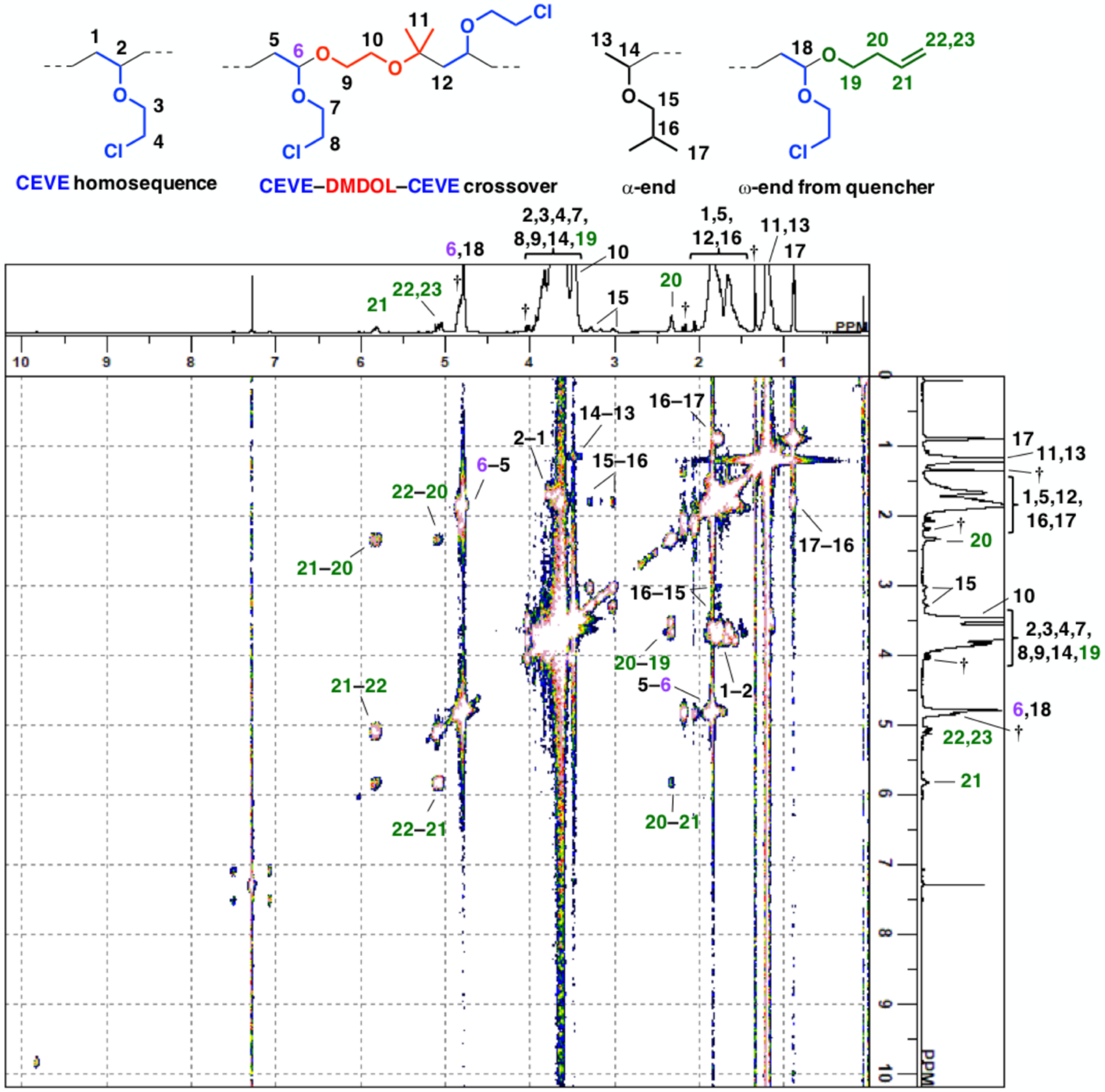


Fig. S4 ^{1}H–^{1}H COSY NMR spectrum of poly(CEVE-*co*-DMDOL) (entry 5 in Table 1) (in $CDCl_3$ at 30 °C).

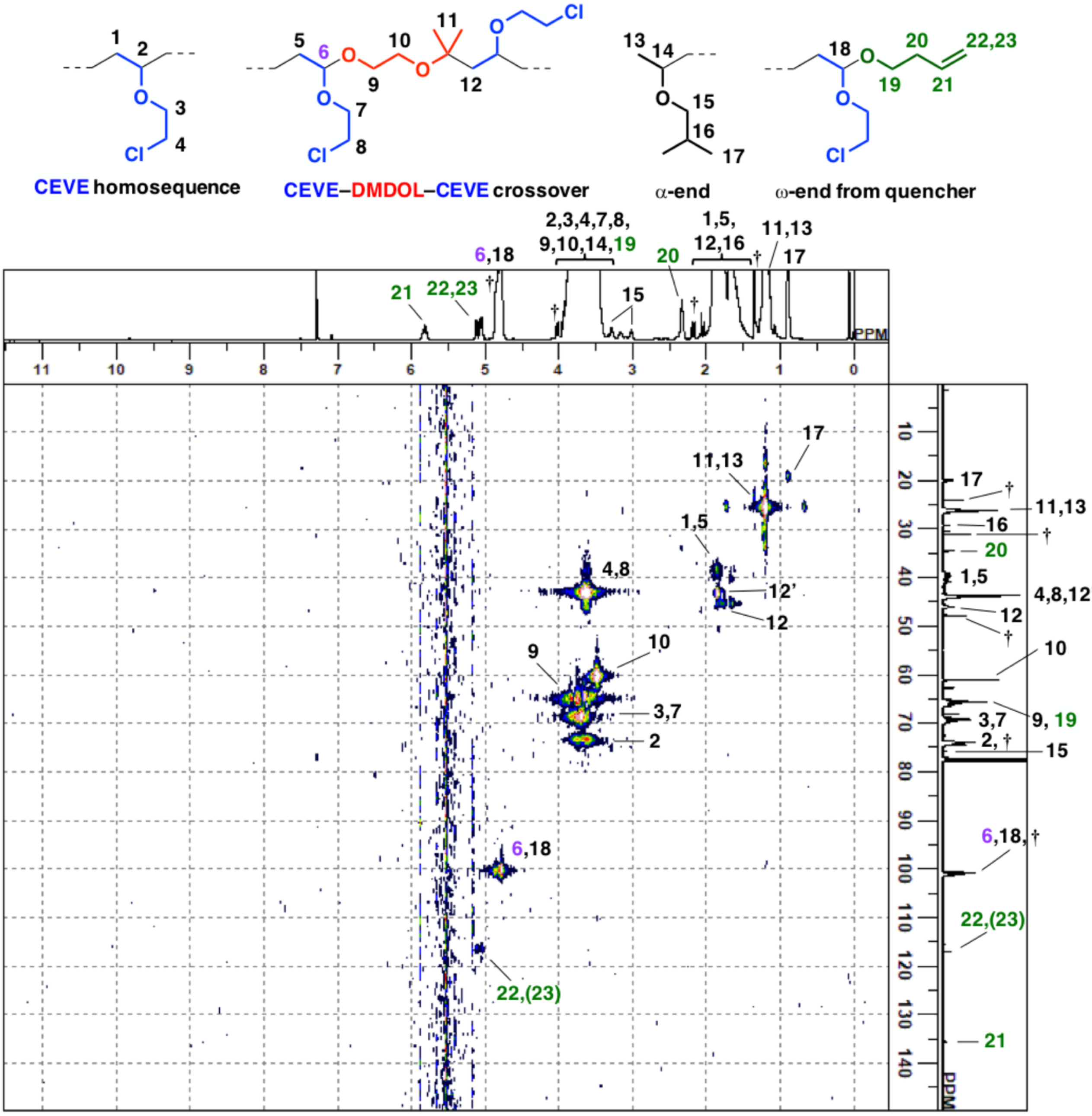


Fig. S5 ^{1}H–^{13}C HSQC NMR spectrum of poly(CEVE-*co*-DMDOL) (entry 5 in Table 1) (in CDCl$_3$ at 30 °C) (see the caption of Figure S6 for peak 12').

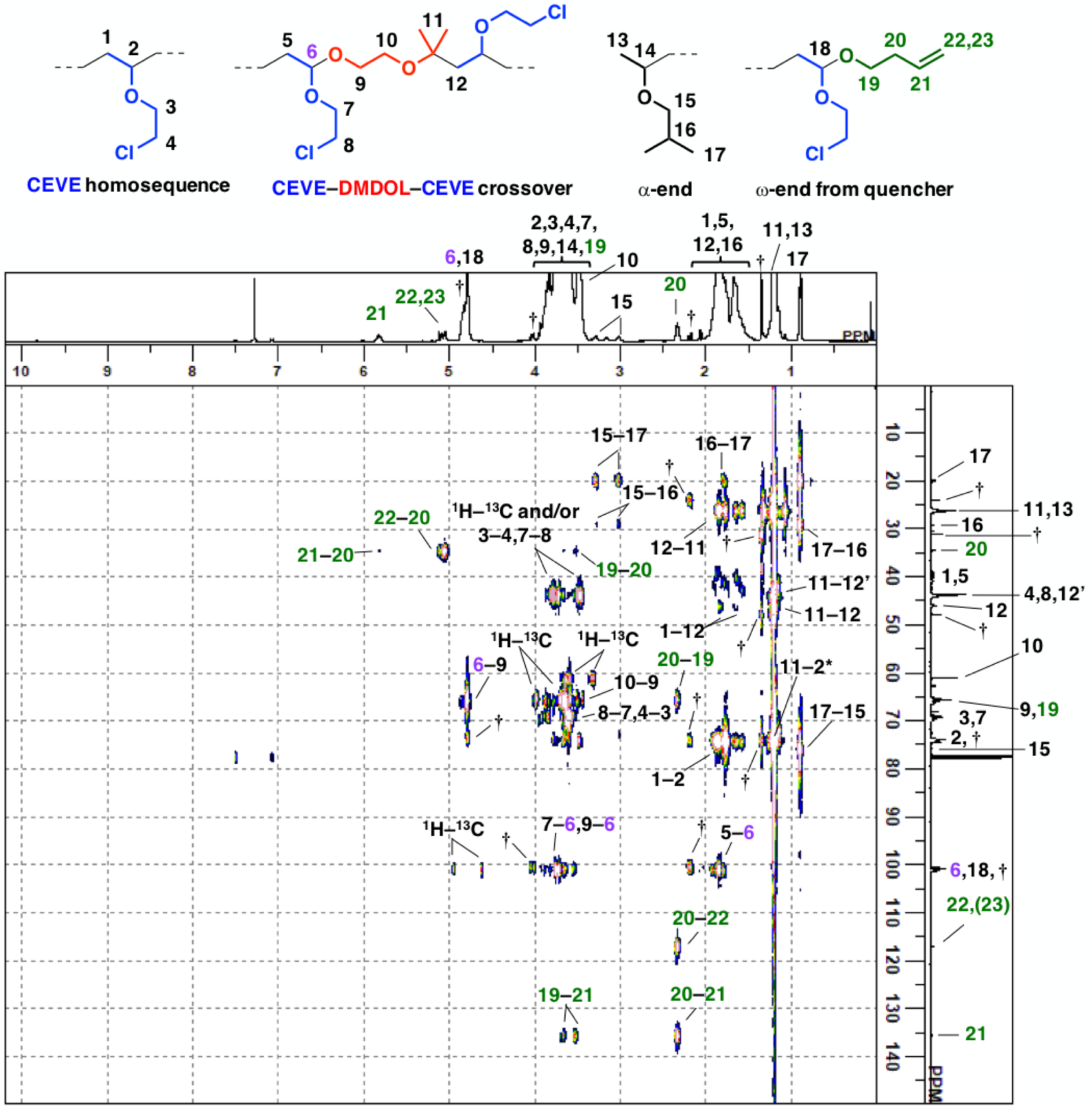
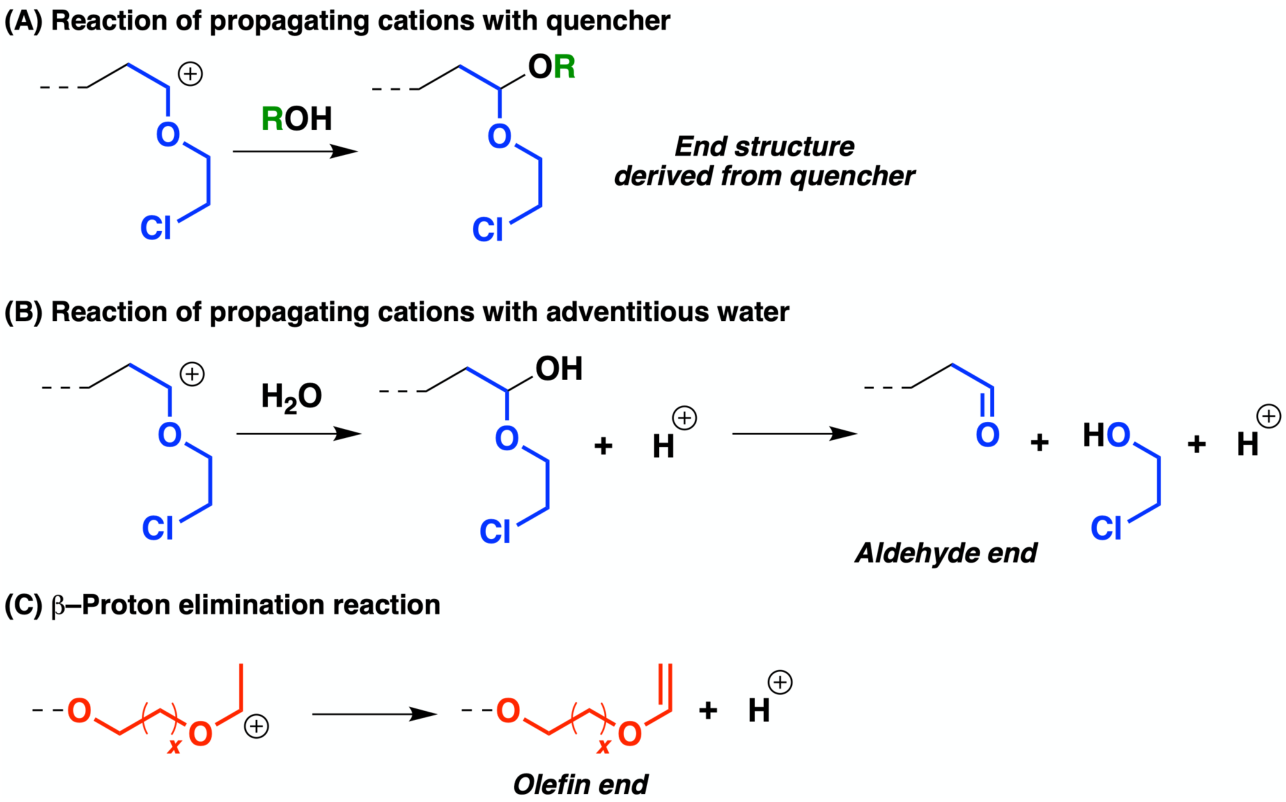


Fig. S6 ^{1}H–^{13}C HMBC NMR spectrum of poly(CEVE-*co*-DMDOL) (entry 5 in Table 1) (in CDCl$_3$ at 30 °C). The peak of the CEVE-derived methylene proton in the main chain of a DMDOL–CEVE–DMDOL sequence likely appears upfield (peak 12’; the overlap with peaks 4 and 8) compared to that of a DMDOL–CEVE–CEVE sequence (peak 12) in the ^{13}C NMR spectrum. * The correlation of 11-2 and/or the correlation between peak 11 and the peak of the quaternary carbon of the DMDOL-derived unit. † A small amount of a side product was likely generated. A possible structure is a cyclic acetal derived from the cyclization reaction of CEVE and DMDOL although the detail is unclear.



Scheme S1 Possible chain end structures.

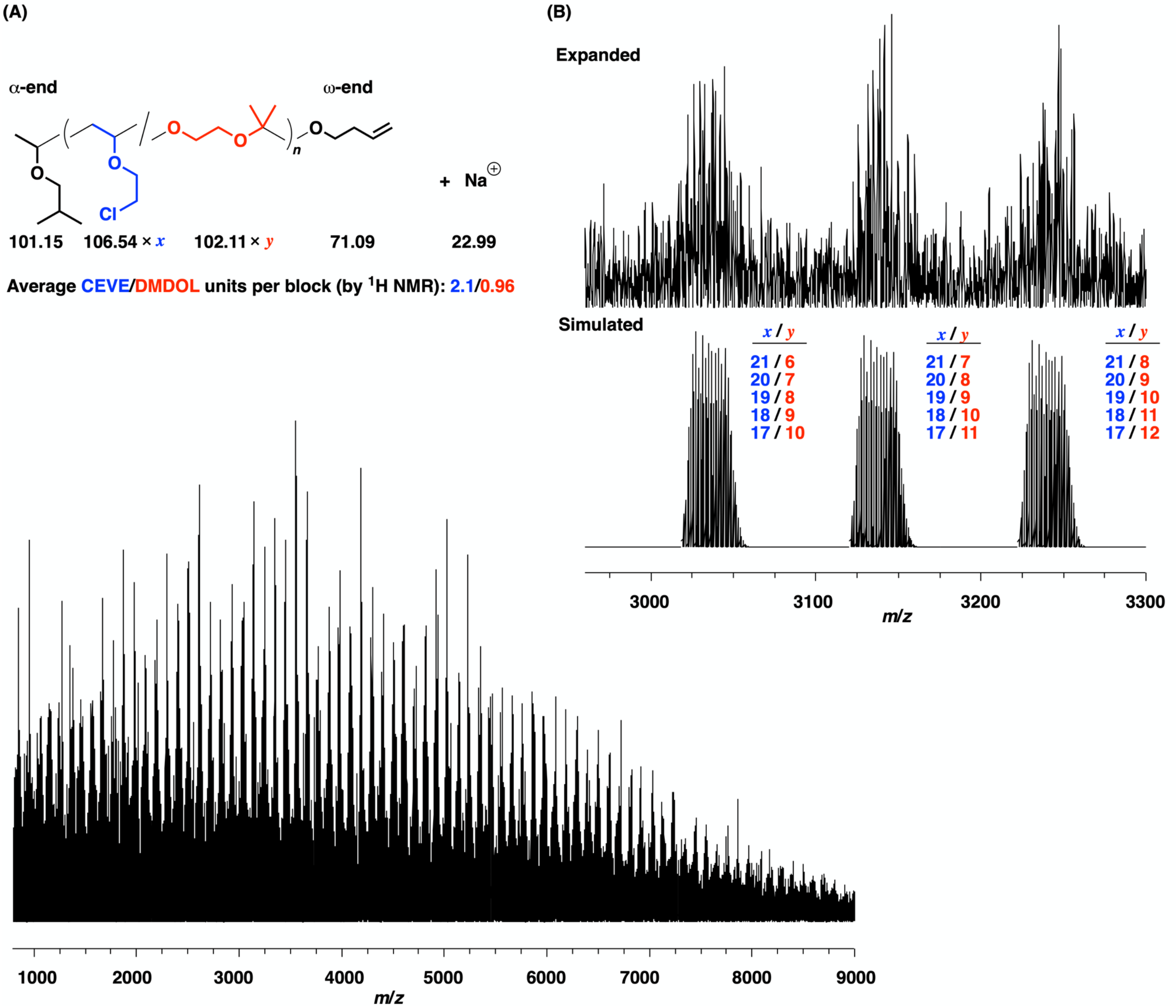


Fig. S7 MALDI-TOF-MS spectrum of the copolymer of CEVE and DMDOL (entry 5 in Table 1): (A) the whole spectrum and (B) the expanded spectrum and the simulated patterns.

Note for Figure S7

The spectrum had a series of peak groups at intervals of an *m*/*z* value of approximately 100. Notably, each peak group had a relatively wide *m*/*z* range. Isotopes of chlorine atoms derived from CEVE and slight differences of the molecular weights of both monomer units (CEVE: 106.55, DMDOL: 102.13) are responsible for the wide *m*/*z* range of each peak group. To analyze the spectrum, peak simulation was conducted. The simulation is based on the structures consisting of an α-end derived from the cationogen, CEVE and DMDOL units, and an ω-end derived from the quencher. The ratio of CEVE and DMDOL units (2.1/0.96), which was determined by ^{1}H NMR, was used for the simulation. For example, simulated peaks at the *m*/*z* range of 3100 to 3200 correspond to a mixture of equal amounts of copolymer chains consisting of 21/7 ($C_{129}H_{237}O_{37}Cl_{21}Na$), 20/8 ($C_{130}H_{240}O_{38}Cl_{20}Na$), 19/9 ($C_{131}H_{243}O_{39}Cl_{19}Na$), 18/10 ($C_{132}H_{246}O_{40}Cl_{18}Na$), and 17/11 ($C_{133}H_{249}O_{41}Cl_{17}Na$) of CEVE/DMDOL units. The observed peak groups had similar patterns to the simulated peak groups, which suggests the generation of copolymers with the fragments derived from the cationogen and the quencher.

Table S1 Cationic copolymerization of CEVE and various cyclic acetals[a]

			conv[b] (%)		units per block[d]	
entry	cyclic	time	vinyl	cyclic	vinyl	cyclic
1	DOL	2 h	82	11(0[c])	—	—
2		27 h	100	18(0[c])	—	—
3	MDOL	2 h	19	9[c]	2.2	0.97
4		70 h	60	31	2.7	0.98
5	DOX	2 h	32	18(0[c])	—	—
6		96 h	100	28(0[c])	—	—
7	MDOX	1 h	59	21	5.6	1.0
8		2 h	68	24	5.1	1.0
9	DMDOX	7 s	44[c]	32[c]	1.4	1.0
10		30 s	84[c]	65[c]	1.3	1.0
11	DOP	23 h	36	75	2.7	2.5
12		44 h	71	92	8.3	12
13	MDOP	0.5 h	29	36	1.5	1.8
14		4 h	61	62	1.5	1.7
15	DMDOP	3 s	63	36	1.7	1.0
16		30 s	91[c]	72	1.7	0.92

[a] [CEVE]$_0$ = 0.40 M, [cyclic acetal]$_0$ = 0.40 M, [IBEA]$_0$ = 4.0 mM, [$TiCl_4$]$_0$ = 5.0 mM, [$SnCl_4$]$_0$ = 20 mM, [DTBP]$_0$ = 10 mM, [ethyl acetate] = 20 mM in toluene/dichloromethane (9/1 v/v) at –78 °C. Entries 2, 4, 5, 8, 10, 12, 14 and 16 correspond to entries 1, 3, 8, 10, 12, 14, 16 and 18 in Table 1, respectively [b] Determined by gas chromatography. [c] Determined by gravimetry and ^{1}H NMR analysis of products. [d] Calculated by ^{1}H NMR analysis.

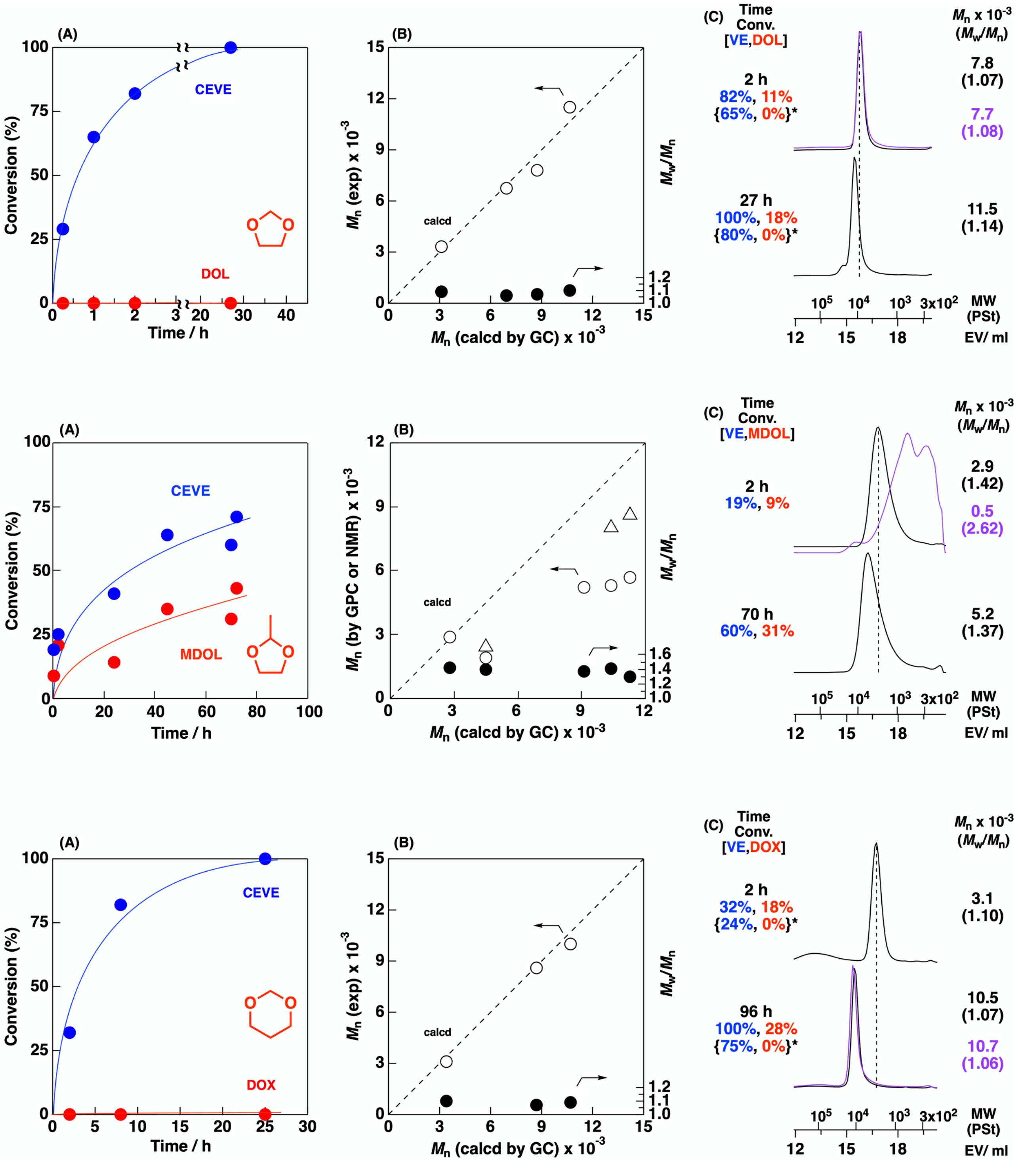


Fig. S8 (A) Time–conversion curves for the copolymerization of CEVE and cyclic acetals, (B) the M_n determined by GPC (open circle) or NMR (triangle; calculated from the integral ratios of the peaks of the main chain and the ω-ends) and M_w/M_n (filled circle) values of the copolymers obtained, and (C) MWD curves of poly(CEVE-*co*-cyclic acetals)s (black) and acid hydrolysis products (purple). Polymerization conditions: $[CEVE]_0 = 0.40$ M, $[\text{cyclic acetals}]_0 = 0.40$ M, $[IBEA]_0 = 4.0$ mM, $[TiCl_4]_0 = 5.0$ mM, $[SnCl_4]_0 = 20$ mM, [ethyl acetate] = 20 mM, $[DTBP]_0 = 10$ mM, in toluene/dichloromethane (9/1 v/v) at –78 °C. Hydrolysis conditions: 1.0 M HCl (aq.) in 1,2-dimethoxyethane (0.5 wt % polymer) at room temperature for 3 h. * Monomer conversion values calculated from gravimetry and ^{1}H NMR of the product.

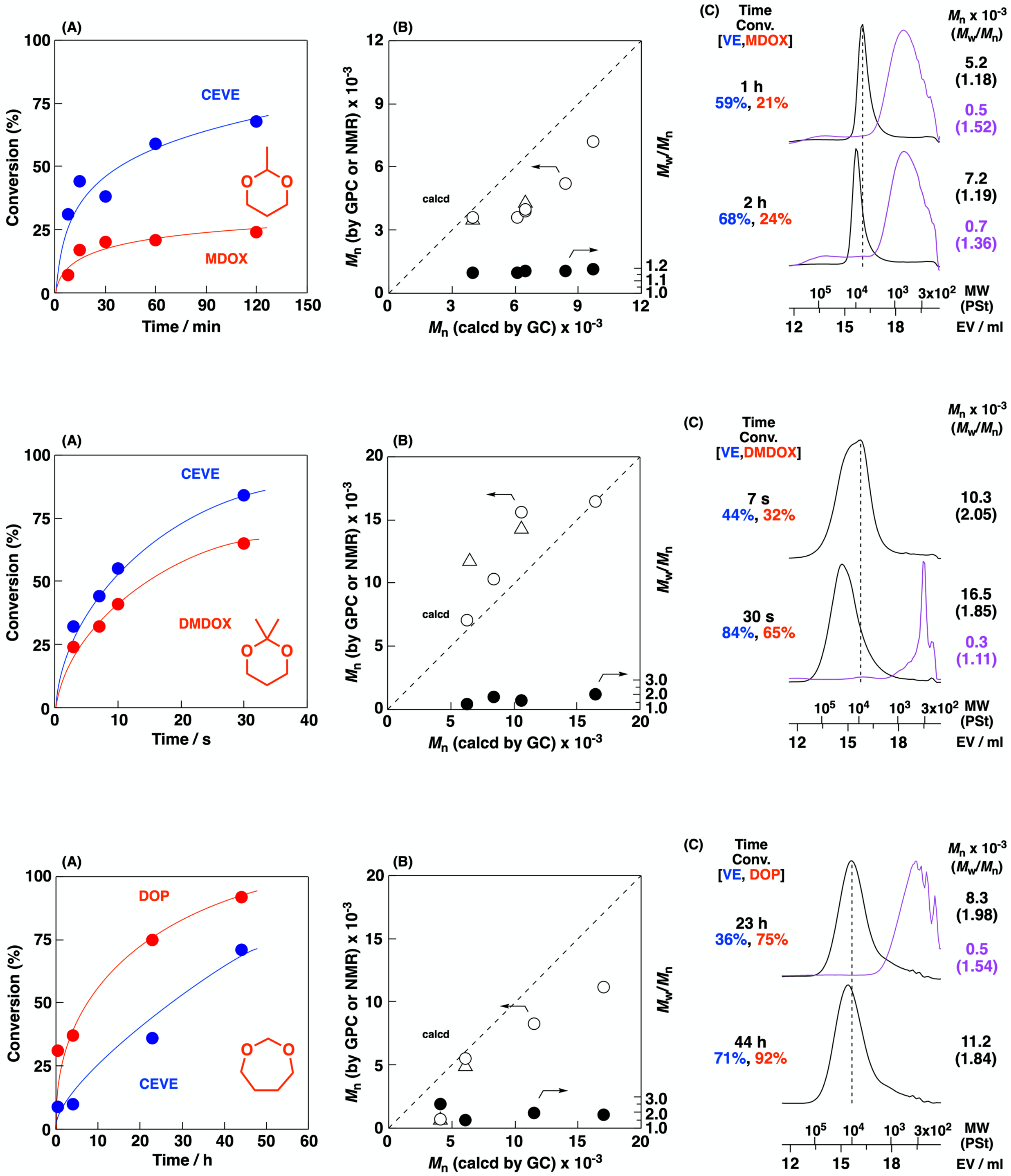


Fig. S8 *(continued)*

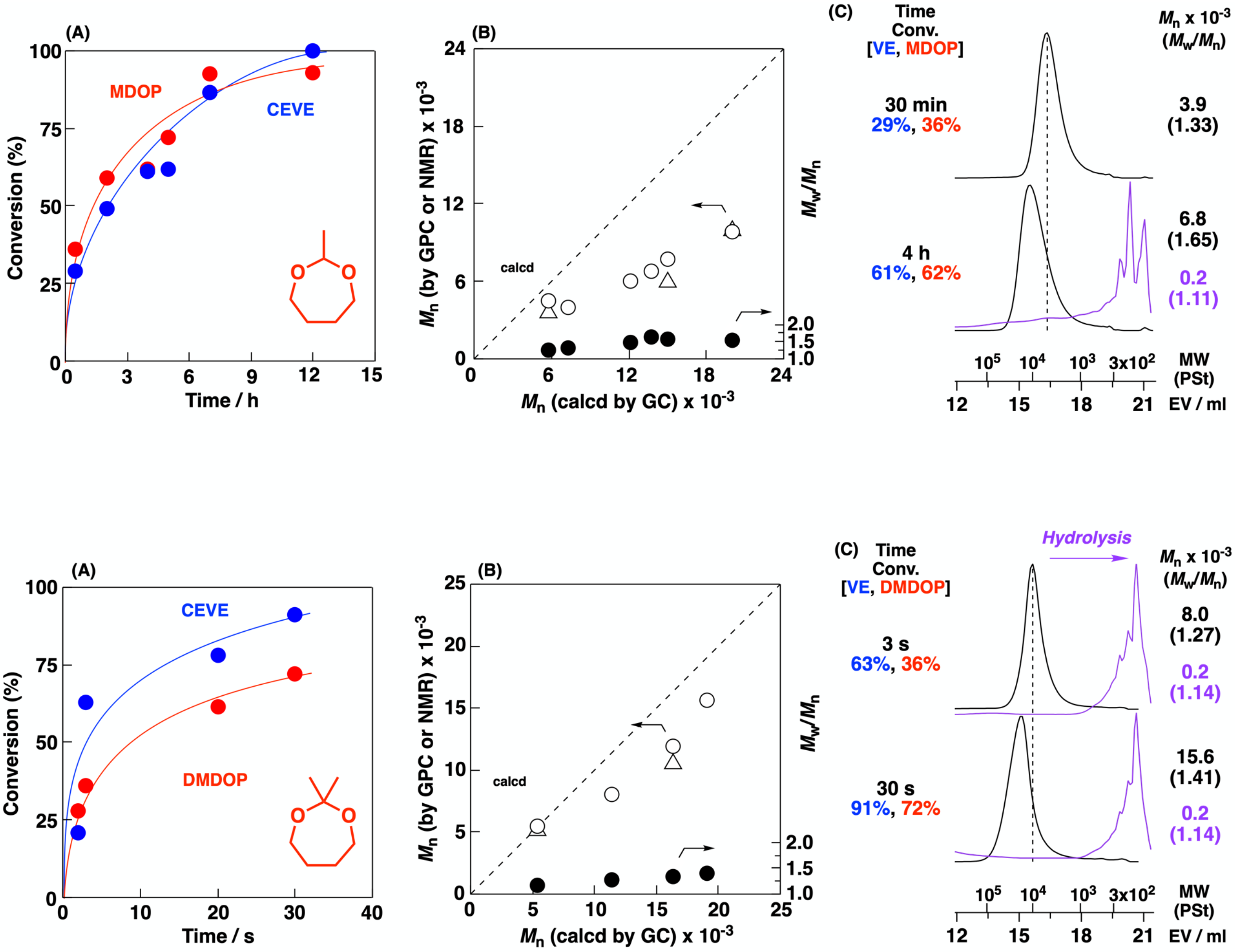


Fig. S8 *(continued)*

Table S2 Chain end analysis for the copolymerization of CEVE and cyclic acetals using 3-buten-1-ol as a quencher[a]

		ω–end (%)[b]	
cyclic	time	3-buten-1-ol	aldehyde
MDOL	0.5 h	81	19
	70 h	82	18
DMDOL	30 s	90	10
	13 min	89	11
MDOX	8 min	70	30
	15 min	64	36
DMDOX	3 s	92	8
	10 s	~100	~0
DOP	30 min	88	12
	4 h	97	3
MDOP	0.5 h	88	12
	4 h	91	9
DMDOP	2 s	98	2
	7 s	83	17

[a] [CEVE]$_0$ = 0.40 M, [cyclic acetal]$_0$ = 0.40 M, [IBEA]$_0$ = 4.0 mM, [TiCl$_4$]$_0$ = 5.0 mM, [SnCl$_4$]$_0$ = 20 mM, [ethyl acetate] = 20 mM, [DTBP]$_0$ = 10 mM in toluene/dichloromethane (9/1 v/v) at –78 °C. [b] Determined by ^{1}H NMR analysis.

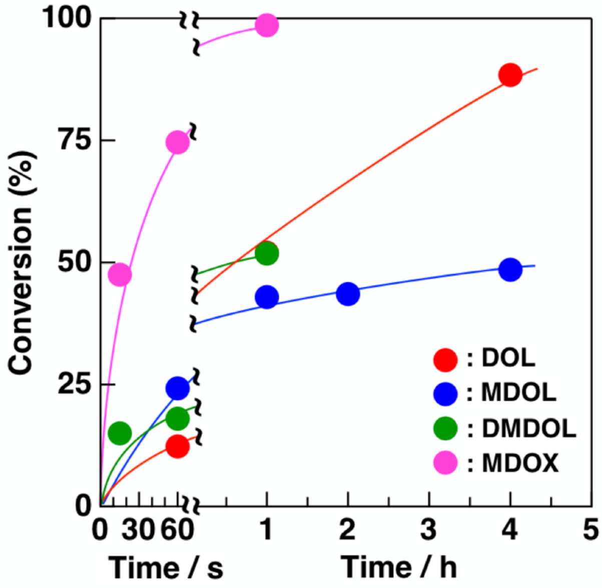


Fig. S9 Time–conversion curves for the polymerization of IBVE using cyclic acetals as a Lewis base additive. Polymerization conditions: [IBVE]$_0$ = 0.76 M, [cyclic acetals]$_0$ = 1.0 M, [IBVE-HCl]$_0$ = 4.0 mM, [SnCl$_4$]$_0$ = 5.0 mM, in toluene at –78 °C.

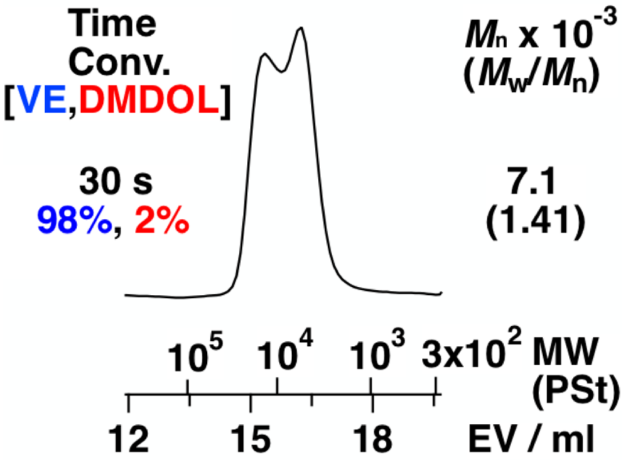


Fig. S10 MWD curves of products obtained via the copolymerization of IBVE and DMDOL. Polymerization conditions: $[\text{IBVE}]_0$ = 0.40 M, $[\text{DMDOL}]_0$ = 0.40 M, $[\text{IBEA}]_0$ = 4.0 mM, $[\text{TiCl}_4]_0$ = 5.0 mM, $[\text{SnCl}_4]_0$ = 20 mM, [ethyl acetate] = 20 mM, $[\text{DTBP}]_0$ = 10 mM, in toluene/dichloromethane (9/1 v/v) at –78 °C.

Table S3 Cationic copolymerization of IBVE and various cyclic acetals[a]

				conv (%)[b]				crossover per chain[d]		units per block[d]	
entry	vinyl	cyclic	time	vinyl	cyclic	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]	V to A[e]	A to V[e]	vinyl	cyclic
1	IBVE	DOL	15 s	48	11(0[f])	5.0	1.13	—	—	—	—
2			30 s	73	14(0[f])	7.1	1.10	—	—	—	—
3	IBVE	MDOL	30 s	46	9(1[f])	5.0	1.15	—	—	—	—
4			60 s	60	4(1[f])	6.7	1.09	—	—	—	—
5	IBVE	DMDOL	30 s	38	0(1[f])	4.4	1.12	1	1	35	1.0
6			3 min	84	0(3[f])	9.9	1.09	3	3	27	1.0
7	IBVE	DOX	30 s	55	0	5.3	1.17	—	—	—	—
8			60 s	68	0	6.4	1.18	—	—	—	—
9	IBVE	MDOX	30 s	43	13(0[f])	4.6	1.10	—	—	—	—
10			60 s	64	3(0[f])	6.8	1.09	—	—	—	—
11	IBVE	DMDOX	10 s	48	11[f]	7.3	1.20	12	12	3.5	0.93
12			30 s	98	24[f]	12.8	1.16	30	30	3.3	0.95
13	IBVE	DOP	6 h	83	8	4.5	1.49	1.5	~0	29	1.5
14			24 h	100	46	5.1	1.34	1.0	~0	40	11
15	IBVE	MDOP	30 s	60	35	7.5	1.22	16	17	3.0	1.4
16			90 s	92	58	8.6	1.36	20	21	2.6	1.4
17	IBVE	DMDOP	10 s	37	9[f]	6.2	1.19	9	9	3.4	1.0
18			30 s	82	28[f]	13.0	1.16	28	28	2.8	1.0

[a] $[\text{IBVE}]_0$ = 0.50 M, $[\text{cyclic acetal}]_0$ = 0.50 M, $[\text{IBVE-HCl}]_0$ = 5.0 mM, $[\text{SnCl}_4]_0$ = 5.0 mM, [ethyl acetate] = 1.0 M in dichloromethane at –78 °C. Entries 2, 4, 6, 8, 10, 12, 13, 16 and 18 correspond to entries 1, 2, 3, 4, 5, 6, 7, 8 and 9 in Table 4, respectively. [b] Determined by gas chromatography. [c] Determined by GPC (polystyrene standards). [d] Estimated by ^{1}H NMR analysis. [e] V: vinyl monomer; A: cyclic acetal. [f] Determined by gravimetry and ^{1}H NMR analysis of products.

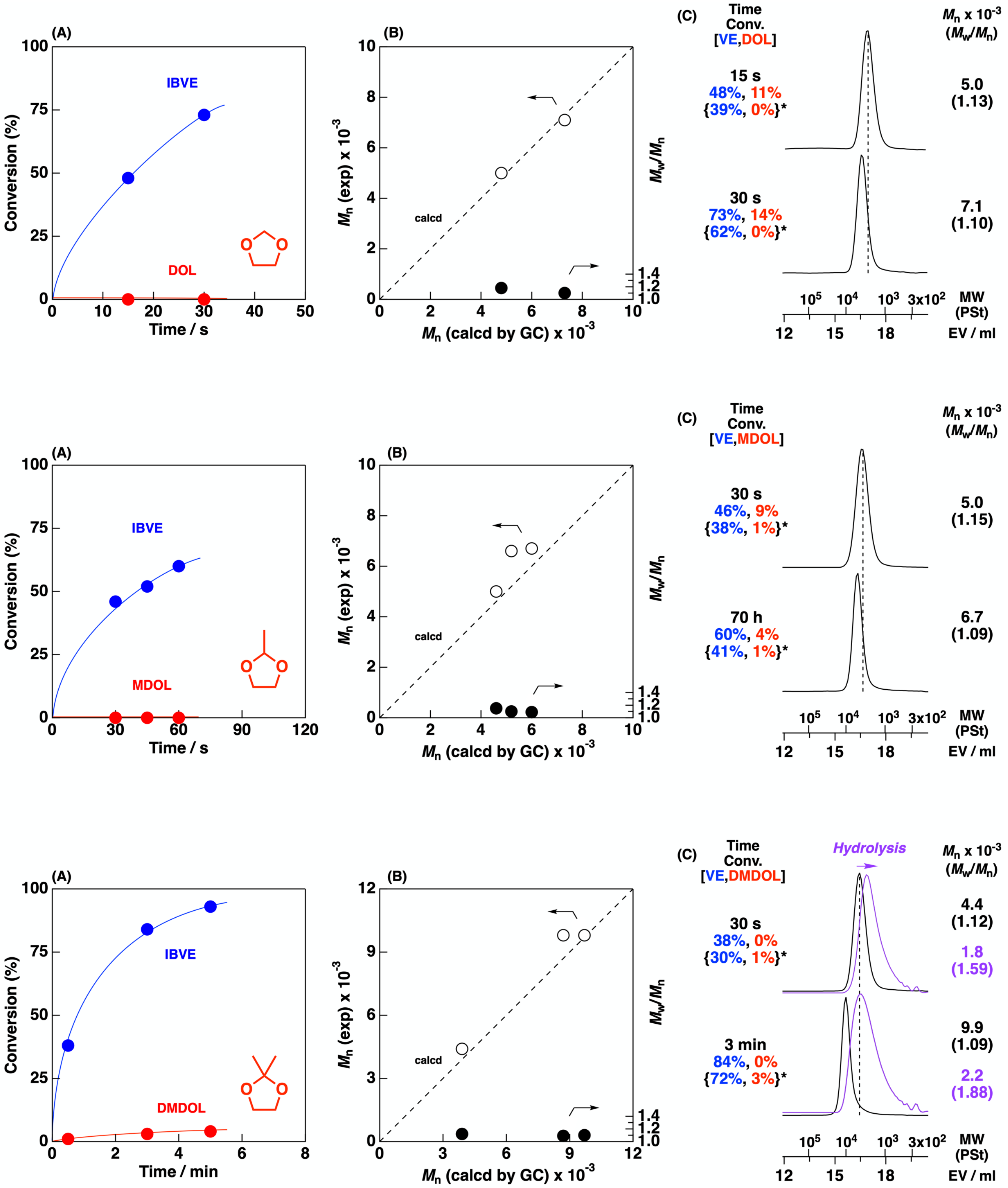


Fig. S11 (A) Time–conversion curves for the copolymerization of IBVE and cyclic acetals, (B) the M_n (open circle) and M_w/M_n (filled circle) values of the copolymers obtained, and (C) MWD curves of poly(IBVE-*co*-cyclic acetals)s (black) and acid hydrolysis products (purple). Polymerization conditions: $[IBVE]_0 = 0.50$ M, $[\text{cyclic acetals}]_0 = 0.50$ M, $[\text{IBVE-HCl}]_0 = 5.0$ mM, $[SnCl_4]_0 = 5.0$ mM, [ethyl acetate] = 1.0 M, in dichloromethane at –78 °C. Hydrolysis conditions: 1.0 M HCl (aq.) in 1,2-dimethoxyethane (0.5 wt % polymer) at room temperature for 3 h. * Monomer conversion values calculated from gravimetry and ^1H NMR of the product.

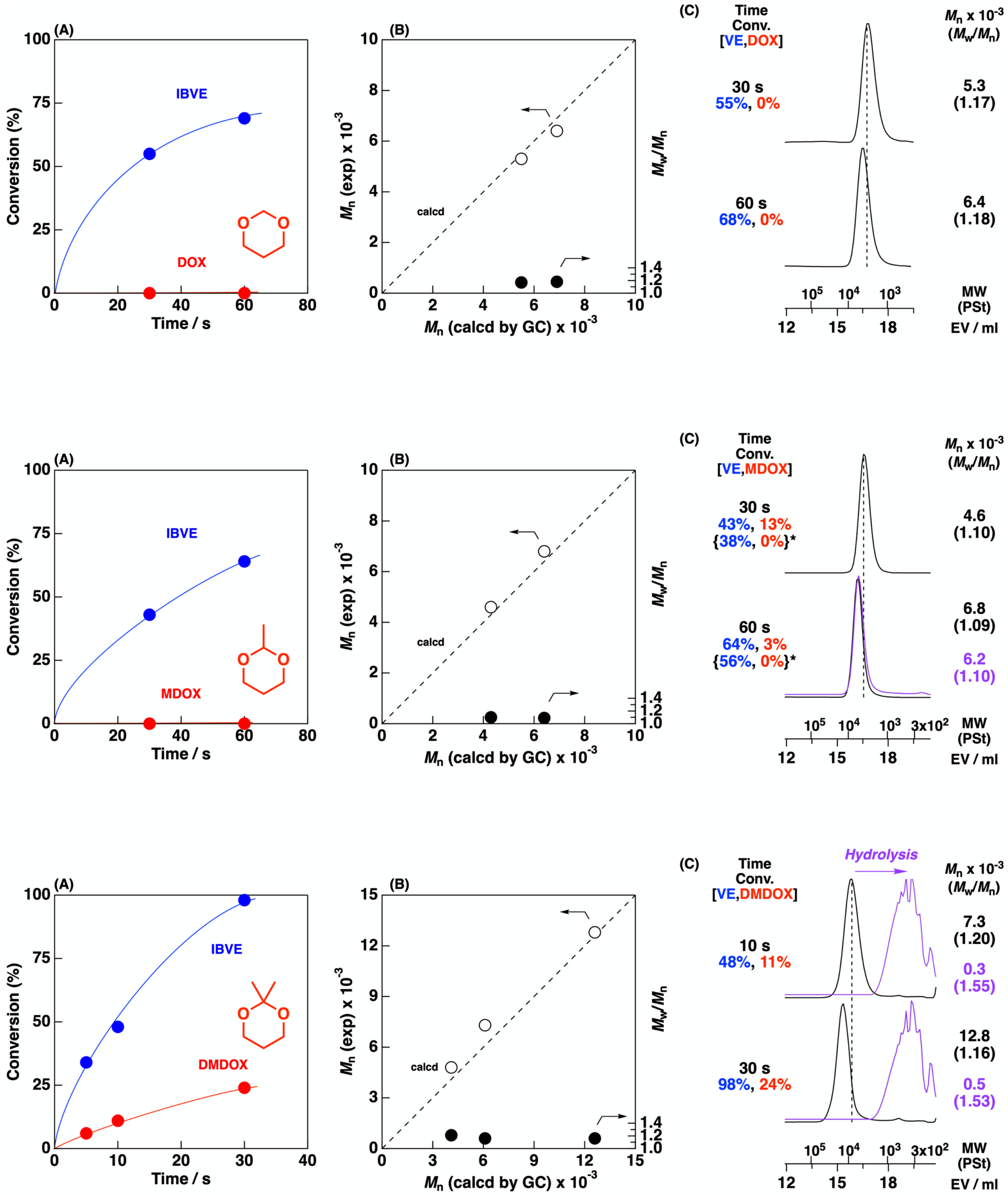


Fig. S11 *(continued)*

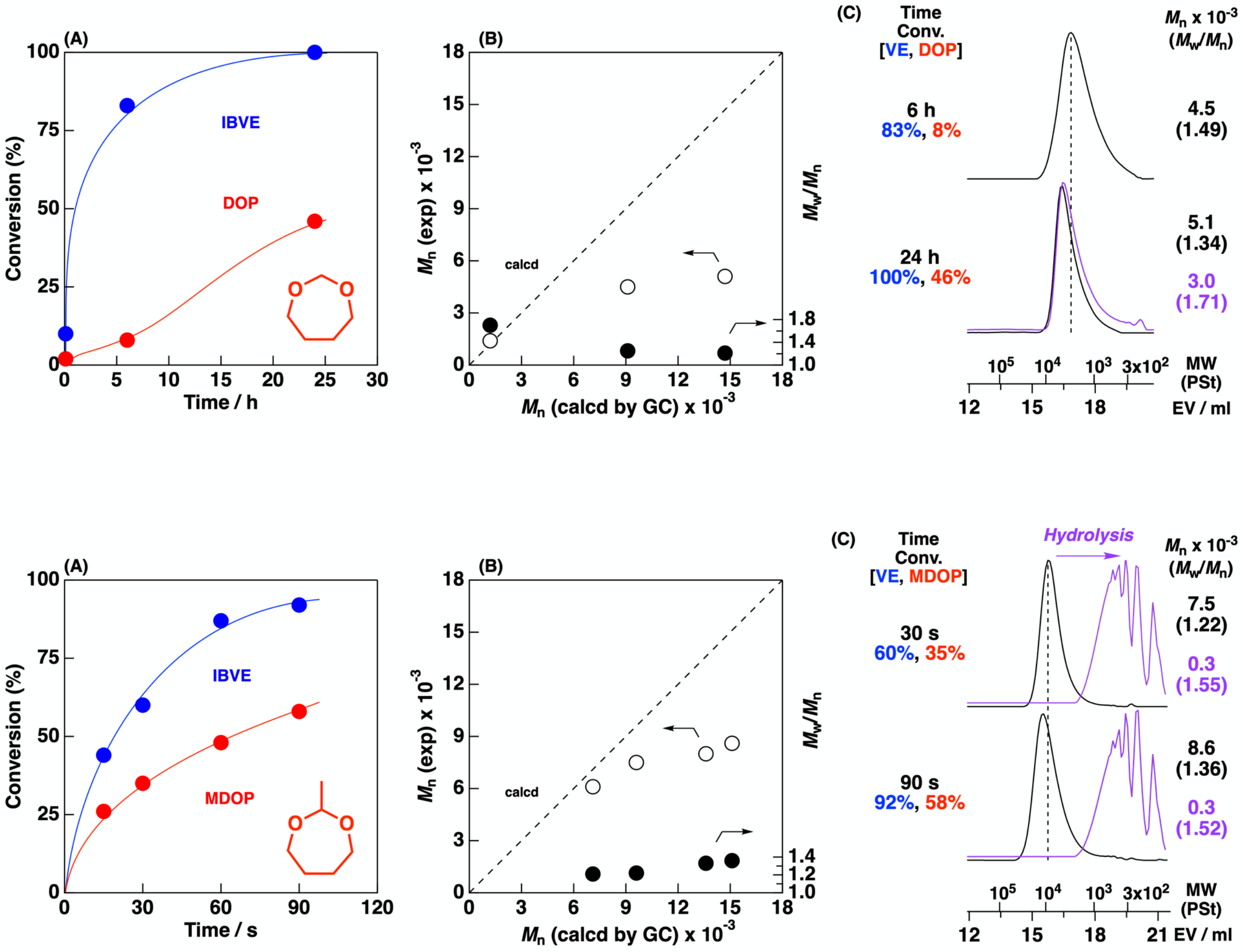


Fig. S11 *(continued)*

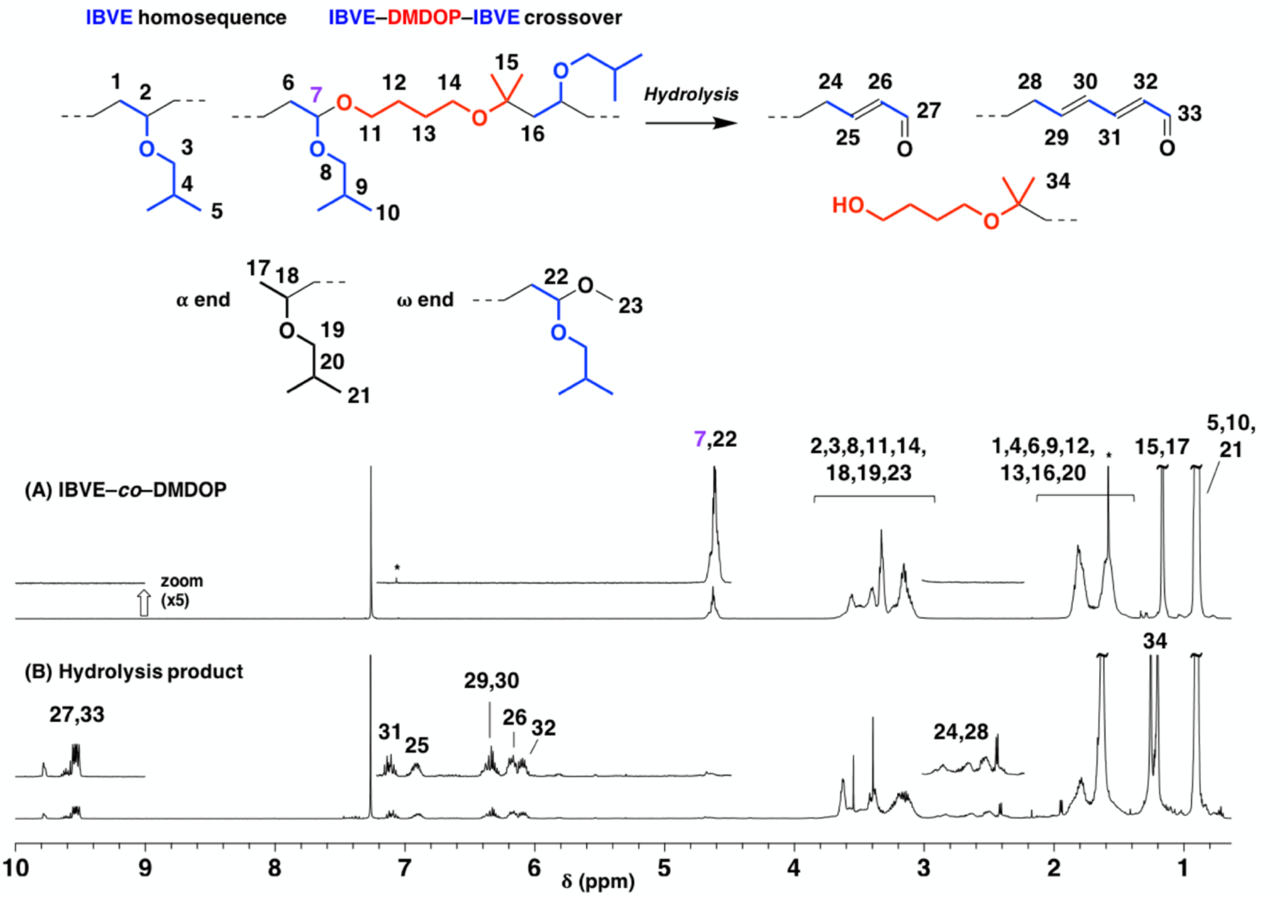


Fig. S12 ^{1}H NMR spectra of (A) poly(IBVE-*co*-DMDOP) (entry 17 in Table S3) and (B) the hydrolysis product (in CDCl$_3$ at 30 °C; * water, satellite, etc).

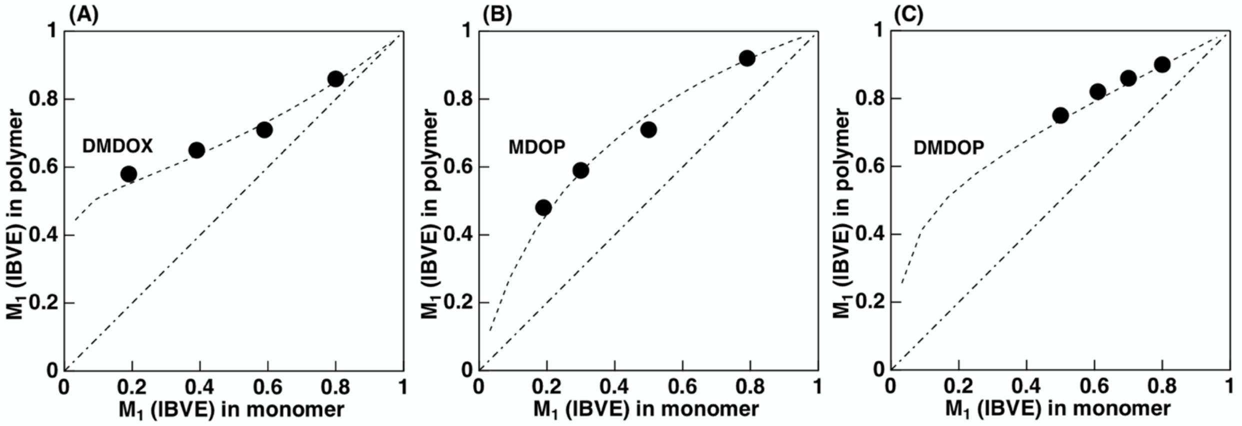


Fig. S13 Copolymer compositions for the cationic copolymerizations of IBVE with (A) DMDOX, (B) MDOP, and (C) DMDOP (broken curves: curves that were drawn using the *r* values obtained by the Kelen–Tüdõs method; dashed-dotted lines: azeotropic lines). Polymerization conditions: [IBVE]$_0$ + [cyclic acetal]$_0$ = 1.0 M, [IBVE–HCl]$_0$ = 5.0 mM, [SnCl$_4$]$_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, in dichloromethane at –78 °C.