

Electronic Supplementary Information:

Sequence-Controlled Degradable Polymers by Controlled Cationic Copolymerization of Vinyl Ethers and Aldehydes: Precise Placement of Cleavable Units at Predetermined Positions

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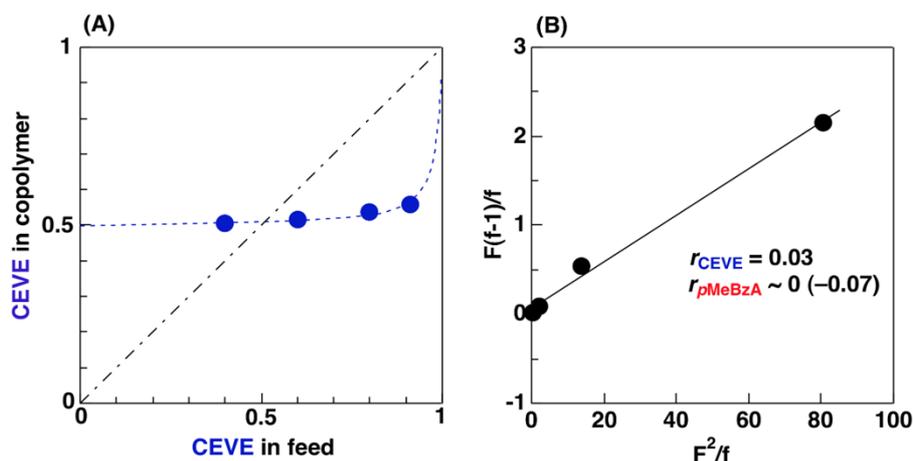


Figure S1. (A) Copolymer composition curves of CEVE with *p*MeBzA and (B) the Fineman-Ross plot for the copolymerization of CEVE with *p*MeBzA. The broken curve shown in Figure S1A was drawn using the r_{CEVE} (0.03) and r_{pMeBzA} (0) values. The dashed-dotted line is an azeotropic line. Polymerization conditions: $[\text{monomer}]_{\text{total}, 0} = 1.2 \text{ M}$, $[\text{EtSO}_3\text{H}]_0 = 8.0 \text{ mM}$, $[\text{GaCl}_3]_0 = 4.0 \text{ mM}$, $[1,4\text{-dioxane}] = 0.50 \text{ M}$, in toluene at $-78 \text{ }^\circ\text{C}$.

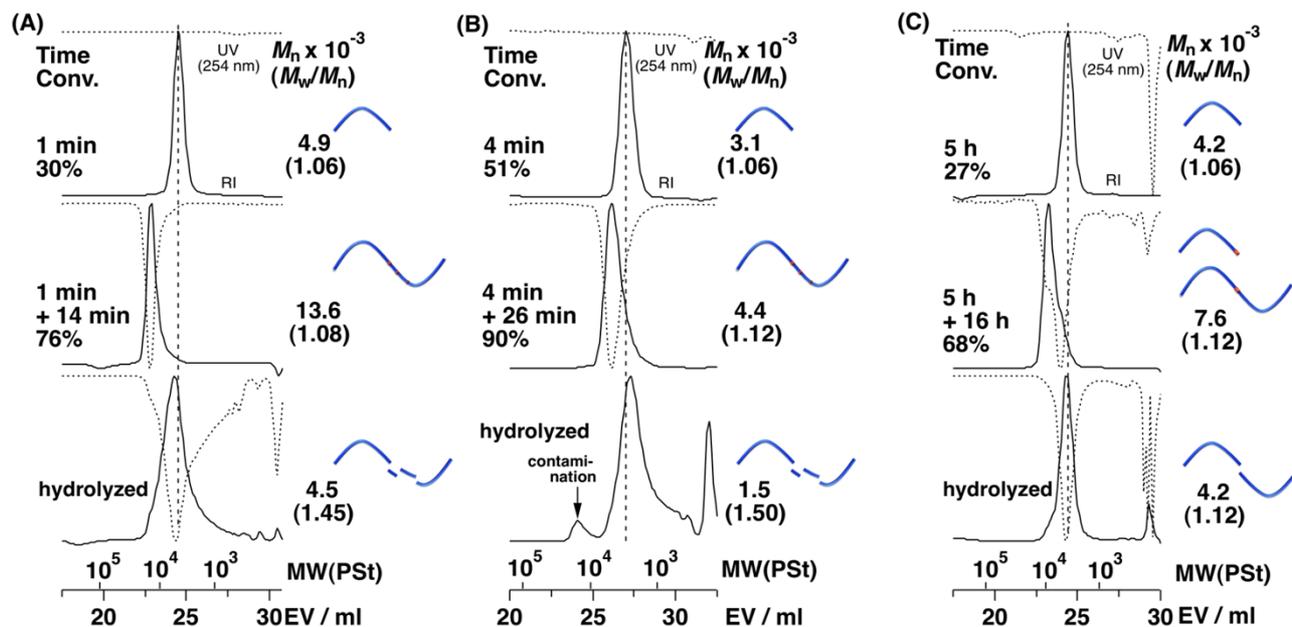


Figure S2. MWD curves of products obtained by the addition of a small amount of aldehyde during the living cationic polymerization of VE (middle) and its acid-hydrolysis product (lower). (A) A combination of IBVE and *p*MeBzA, (B) a combination of IBVE and myrtenal, and (C) a combination of CEVE and myrtenal. Polymerization: $[\text{VE}]_0 = 0.40$ (for B) or 1.2 (for A and C) M, $[\text{aldehyde}]_{\text{added}} = 40 \text{ mM}$ (five equivalent toward propagating chain), $[\text{EtSO}_3\text{H}]_0 = 8.0 \text{ mM}$, $[\text{GaCl}_3]_0 = 4.0 \text{ mM}$, $[1,4\text{-dioxane}] = 0.50$ (for A and C) or 1.0 (for B) M, in toluene at $-78 \text{ }^\circ\text{C}$; hydrolysis conditions: 0.50 M aqueous HCl–1,2-dimethoxyethane at room temperature for 2 h, $0.33 \text{ wt}\%$.

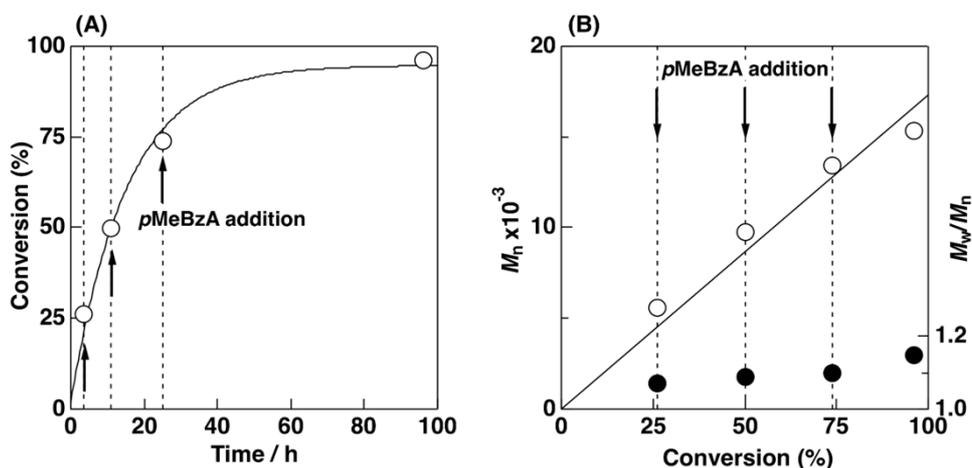


Figure S3. (A) Time–conversion curves and (B) M_n and M_w/M_n values of products obtained by the multiple addition of small amounts of *p*MeBzA during the living cationic polymerization of CEVE. Polymerization conditions: $[CEVE]_0 = 1.2$ M, $[pMeBzA]_{added} = 40$ mM (five equivalent toward propagating chain), $[EtSO_3H]_0 = 8.0$ mM, $[GaCl_3]_0 = 4.0$ mM, $[1,4\text{-dioxane}] = 0.50$ M, in toluene at -78 °C.

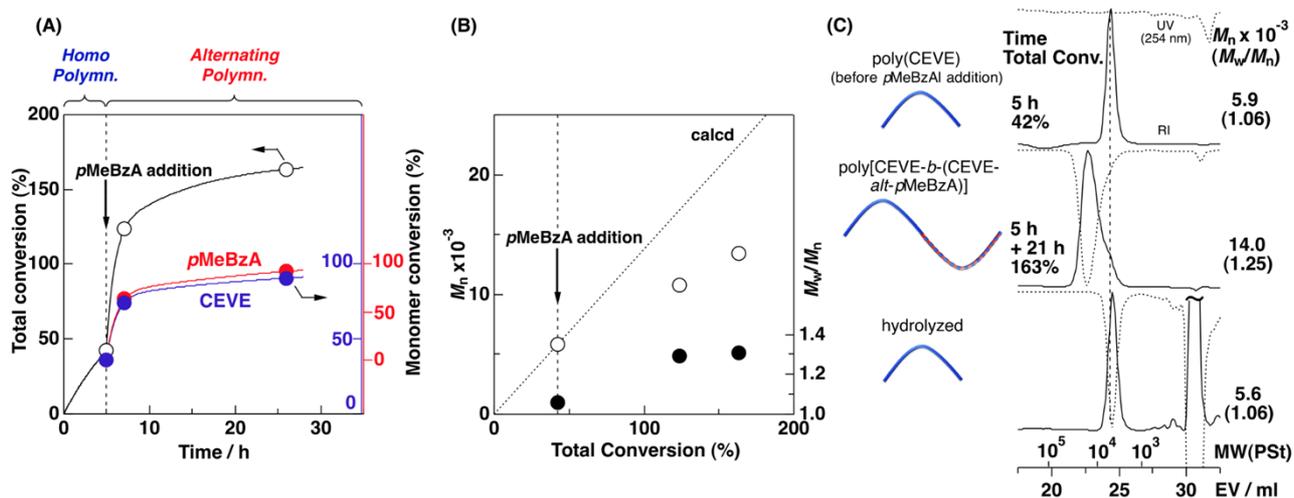


Figure S4. (A) Time–conversion curves, (B) M_n and M_w/M_n values, and (C) MWD curves of a product obtained by the addition of a large amount of *p*MeBzA during the living cationic polymerization of CEVE and its acid-hydrolysis product. Polymerization conditions: $[CEVE]_0 = 1.2$ M, $[pMeBzA]_{added} = 0.78$ M, $[EtSO_3H]_0 = 8.0$ mM, $[GaCl_3]_0 = 4.0$ mM, $[1,4\text{-dioxane}] = 1.0$ M, in toluene at -78 °C; hydrolysis conditions: 0.50 M aqueous HCl–1,2-dimethoxyethane at room temperature for 2 h, 0.33 wt%.

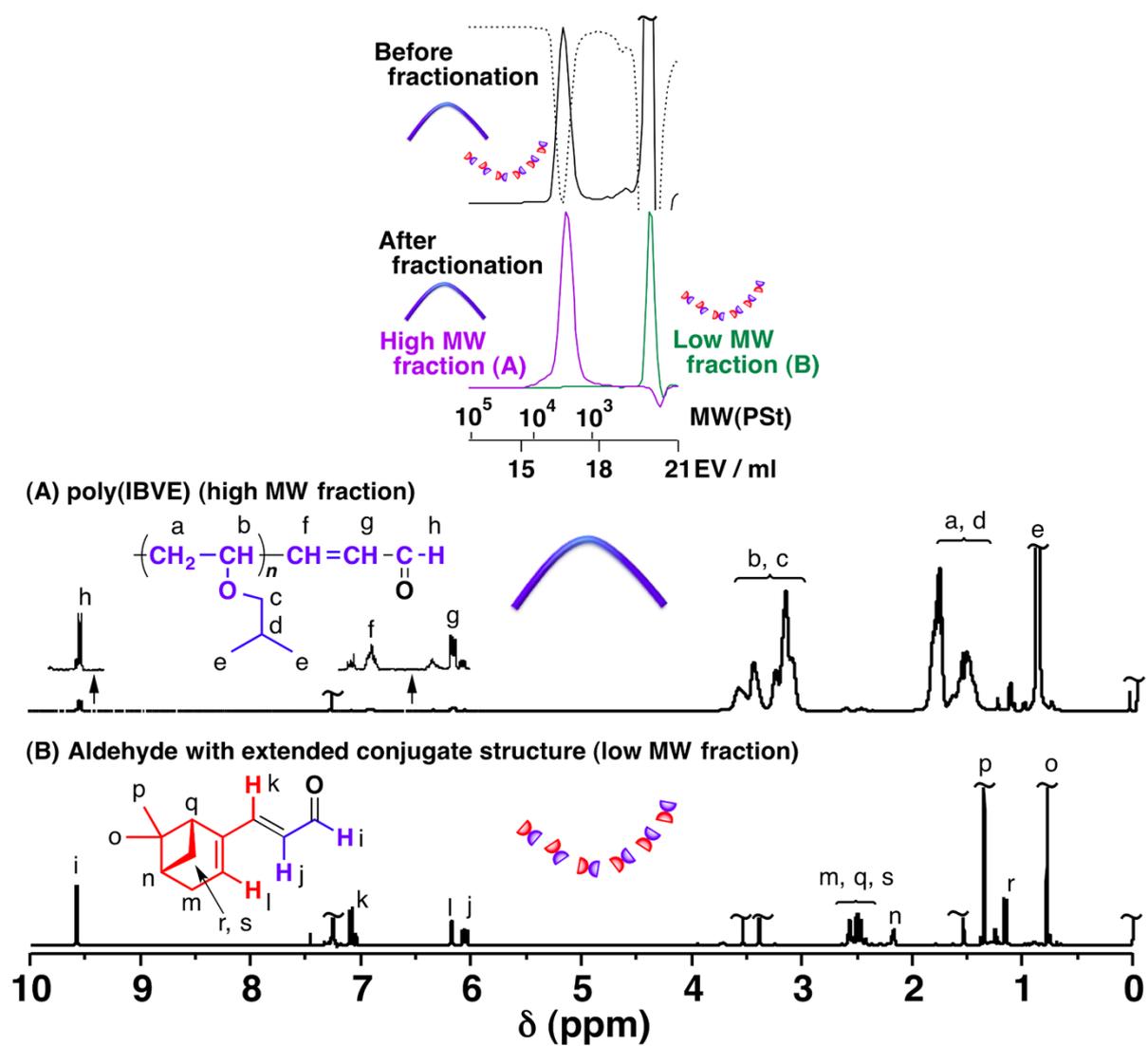


Figure S5. GPC fractionation analyses of poly[IBVE-*b*-(IBVE-*alt*-myrtenal)]: MWD curves before and after fractionation and ¹H NMR spectra of each fraction. See also Figure 4.