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: [monomer]\(_{\text{total}}\) \(_0\) = 1.2 M, [EtSO\(_3\)H] \(_0\) = 8.0 mM, [GaCl\(_3\)] \(_0\) = 4.0 mM, [1,4-dioxane] = 0.50 M, in toluene at –78 °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: [VE] \(_0\) = 0.40 (for B) or 1.2 (for A and C) M, [aldehyde] \(_{\text{added}}\) = 40 mM (five equivalent toward propagating chain), [EtSO\(_3\)H] \(_0\) = 8.0 mM, [GaCl\(_3\)] \(_0\) = 4.0 mM, [1,4-dioxane] = 0.50 (for A and C) or 1.0 (for B) 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 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 pMeBzA during the living cationic polymerization of CEVE. Polymerization conditions: $[\text{CEVE}]_0 = 1.2$ M, $[\text{pMeBzA}]_{\text{added}} = 40$ mM (five equivalent toward propagating chain), $[\text{EtSO}_3\text{H}]_0 = 8.0$ mM, $[\text{GaCl}_3]_0 = 4.0$ mM, $[\text{1,4-dioxane}] = 0.50$ M, in toluene at $–78$ ºC.

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 pMeBzA during the living cationic polymerization of CEVE and its acid-hydrolysis product. Polymerization conditions: $[\text{CEVE}]_0 = 1.2$ M, $[\text{pMeBzA}]_{\text{added}} = 0.78$ M, $[\text{EtSO}_3\text{H}]_0 = 8.0$ mM, $[\text{GaCl}_3]_0 = 4.0$ mM, $[\text{1,4-dioxane}] = 1.0$ M, in toluene at $–78$ ºC; 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 $^1$H NMR spectra of each fraction. See also Figure 4.