

# Supporting Information

## Controlled Cationic Alternating Copolymerization of Benzaldehydes with Vinyl Ethers: Precision Synthesis and Quantitative Degradation to Cinnamaldehydes

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## Experimental Section

**Materials.** Isobutyl vinyl ether (IBVE; TCI), 2-chloroethyl vinyl ether (CEVE; TCI), and dichloromethane (Nacalai) were distilled twice over calcium hydride before use. 1,4-Dioxane (Wako) was distilled over calcium hydride and then lithium aluminum hydride. Toluene and hexane were dried by passage through solvent purification columns (Glass Contour). Benzaldehyde (BzA; Wako), *p*-methoxyBzA (*p*MeOBzA; Nacalai), and 2,6-di-*tert*-butylpyridine (DTBP; Aldrich) were distilled twice over calcium hydride under reduced pressure before use. Ethanesulfonic acid ( $\text{EtSO}_3\text{H}$ ; Aldrich, 95%) was used as received. Solid  $\text{GaCl}_3$  (Aldrich, 99.999%) was dissolved in hexane just before use. Hydrochloric acid (Nacalai) and tetrahydrofuran (THF; Wako) for acid hydrolysis were used as received.

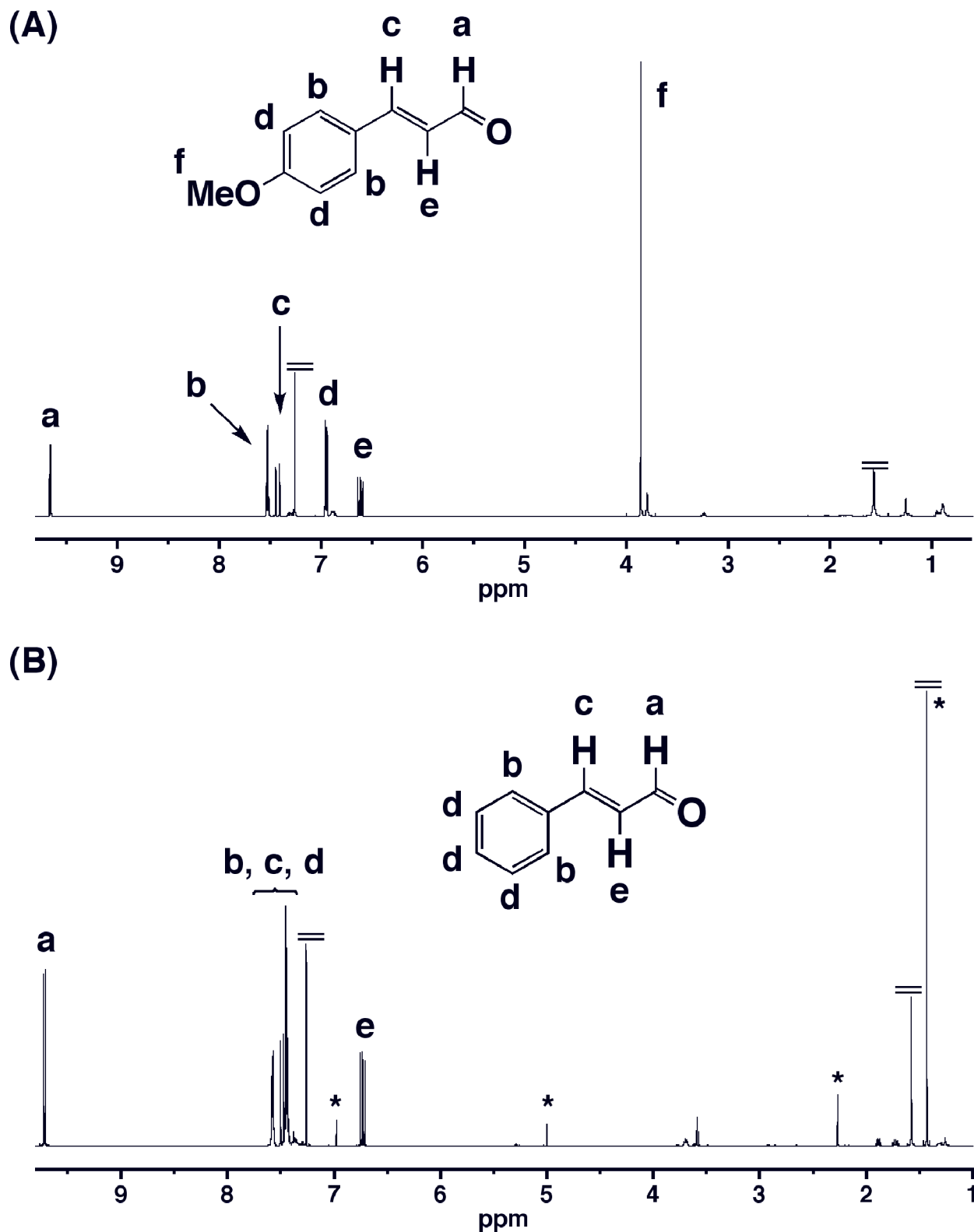
All chemicals except for toluene, hexane, THF, and hydrochloric acid were stored in brown ampules under dry nitrogen.

**Polymerization Procedures.** Polymerization was carried out under a dry nitrogen atmosphere in a baked glass tube equipped with a three-way stopcock. Prechilled EtSO<sub>3</sub>H solution was added to prechilled mixture of monomers, added base, and solvent at 0 °C. The reaction was started by the addition via dry medical syringe of a prechilled Lewis acid solution (0.5 mL) to a prechilled mixture (4.5 mL) of monomers, added base, initiator, and solvent at -78 °C. The reaction mixture was magnetically stirred throughout the polymerization. The polymerization was quenched with prechilled methanol containing a small amount of ammonia solution (3.0 mL; 0.1%). The quenched reaction mixture was diluted with dichloromethane and then washed with water to remove the initiator residues. Solvent and other volatiles were then evaporated under reduced pressure, and the residue was vacuum-dried for at least 6 h at 50 °C. The monomer conversion was determined by a gravimetric method and <sup>1</sup>H NMR analysis.

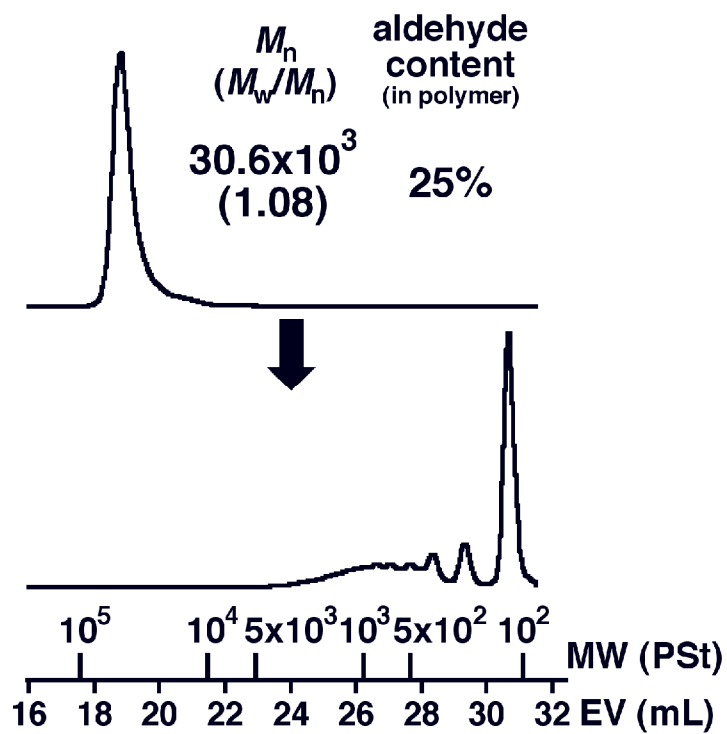
**Acid Hydrolysis.** The copolymer (30 mg) was dissolved in THF (5.0 mL), then the reaction was started by the addition of a mixture of HCl and THF (1.0 M; 5.0 mL). The reaction mixture was magnetically stirred with a stirring bar at 30 °C throughout the hydrolysis. The hydrolysis was quenched with aqueous sodium hydroxide (1.0 M). The quenched reaction mixture was diluted with dichloromethane, washed with water to remove the resulting salt, and the volatiles were evaporated under reduced pressure. The residue was vacuum-dried at room temperature.

**Characterization.** The Molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C with three polystyrene gel columns (TSK gel G-4000H<sub>XL</sub>, G-3000H<sub>XL</sub>, and G-2000H<sub>XL</sub>; 7.8 mm internal diameter × 300 mm; flow rate = 1.0 mL/min) connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive index detector. The number-average molecular weight ( $M_n$ ) and polydispersity ratio [weight-average molecular weight/number-average molecular weight ( $M_w/M_n$ )] were calculated from the chromatographs with respect to 16 polystyrene standards (Tosoh;  $292-1.09 \times 10^6$ ,  $M_w/M_n \leq 1.1$ ). <sup>1</sup>H

NMR spectrum was recorded at 30 °C in CDCl<sub>3</sub> using a JEOL JNM-EX 270 spectrometer (270 MHz), a Varian Mercury 300 spectrometer (300 MHz), a JEOL JNM-LA 500 spectrometer (500 MHz), or a JEOL ECA 500 spectrometer (500 MHz). Differential Scanning Calorimeter (DSC EXSTER-6000, Seiko Instruments Inc.) was operated to determine the glass transition temperature ( $T_g$ ) in the range from -100 to 120 °C for poly(BzAs-*co*-VEs). The heating and cooling rates were 10 °C/min. The  $T_g$  of the copolymer was defined as the temperature of the midpoint of a heat capacity change on the second heating scan. IR spectrum was recorded on a Bio Rad EXCALIBUR FTS-3000 FTIR spectrometer using a KBr disc.

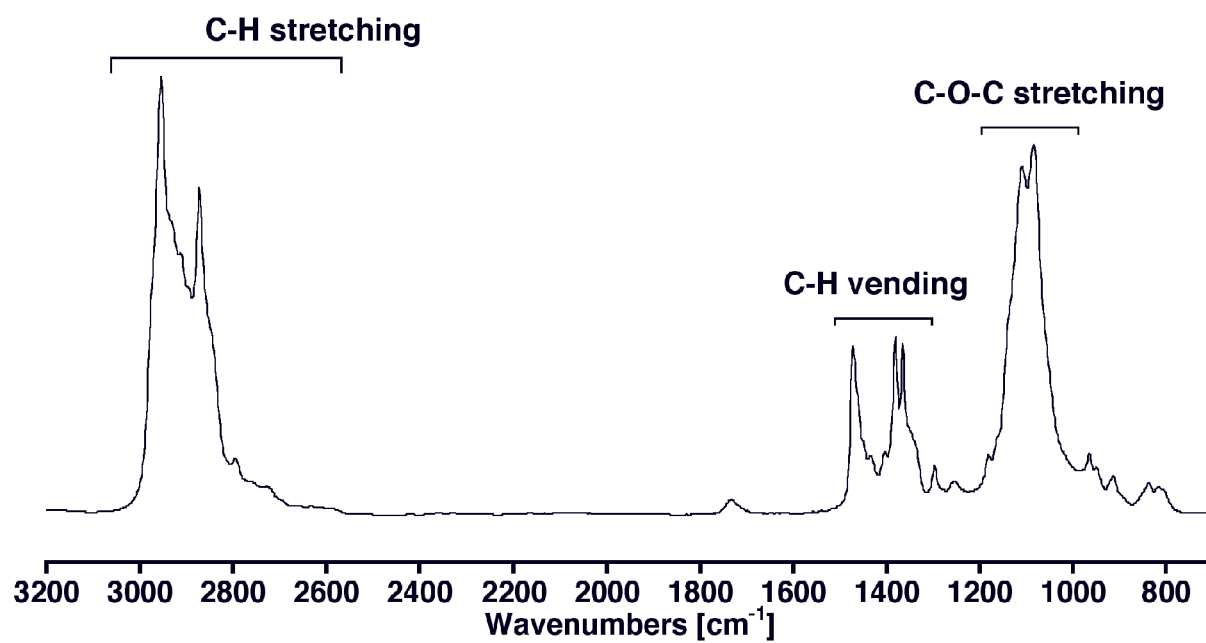


**Figure S1.**  $^1\text{H}$  NMR spectra of hydrolysis products; (A) poly(*p*-methoxybenzaldehyde-*co*-isobutyl vinyl ether) and (B) poly(benzaldehyde-*co*-2-chloroethyl vinyl ether).<sup>1</sup> (Hydrolysis condition: 0.5 N aqueous HCl-tetrahydrofuran (THF) at 30 °C for 2 h.: \*2,6-di-*tert*-butyl-*p*-cresol as a stabilizer in THF.)

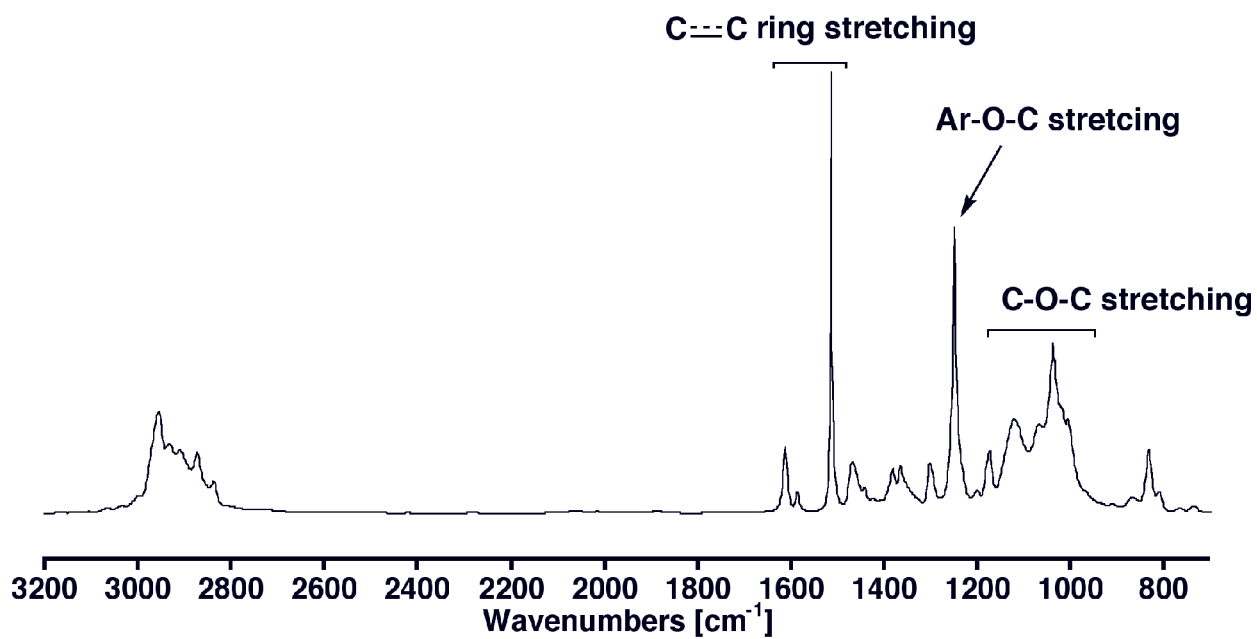


**Figure S2.** Molecular weight distribution curves of poly(benzaldehyde-*co*-isobutyl vinyl ether) (upper, isolated) and hydrolysis products (lower). (Hydrolysis condition: 0.5 N aqueous HCl-tetrahydrofuran at 30 °C for 2 h.)

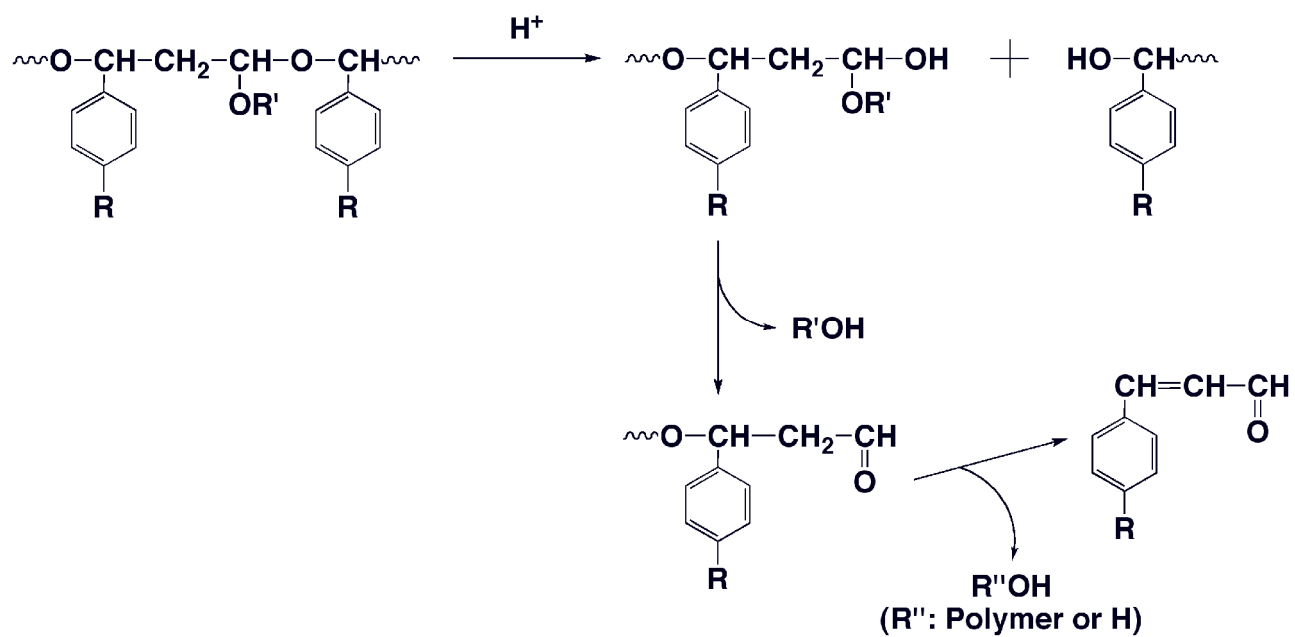
**(A) poly(IBVE)**



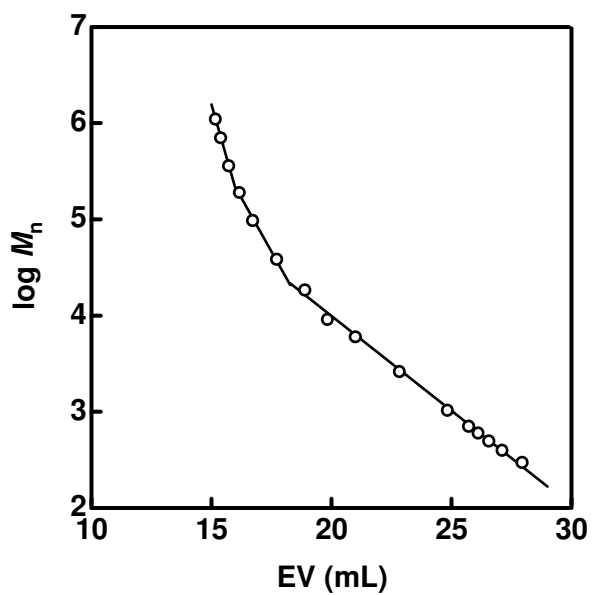
**(B) poly(*p*MeOBzA-co-IBVE)**



**Figure S3.** IR spectra of (A) poly(isobutyl vinyl ether) and (B) poly(*p*-methoxybenzaldehyde-co-isobutyl vinyl ether).

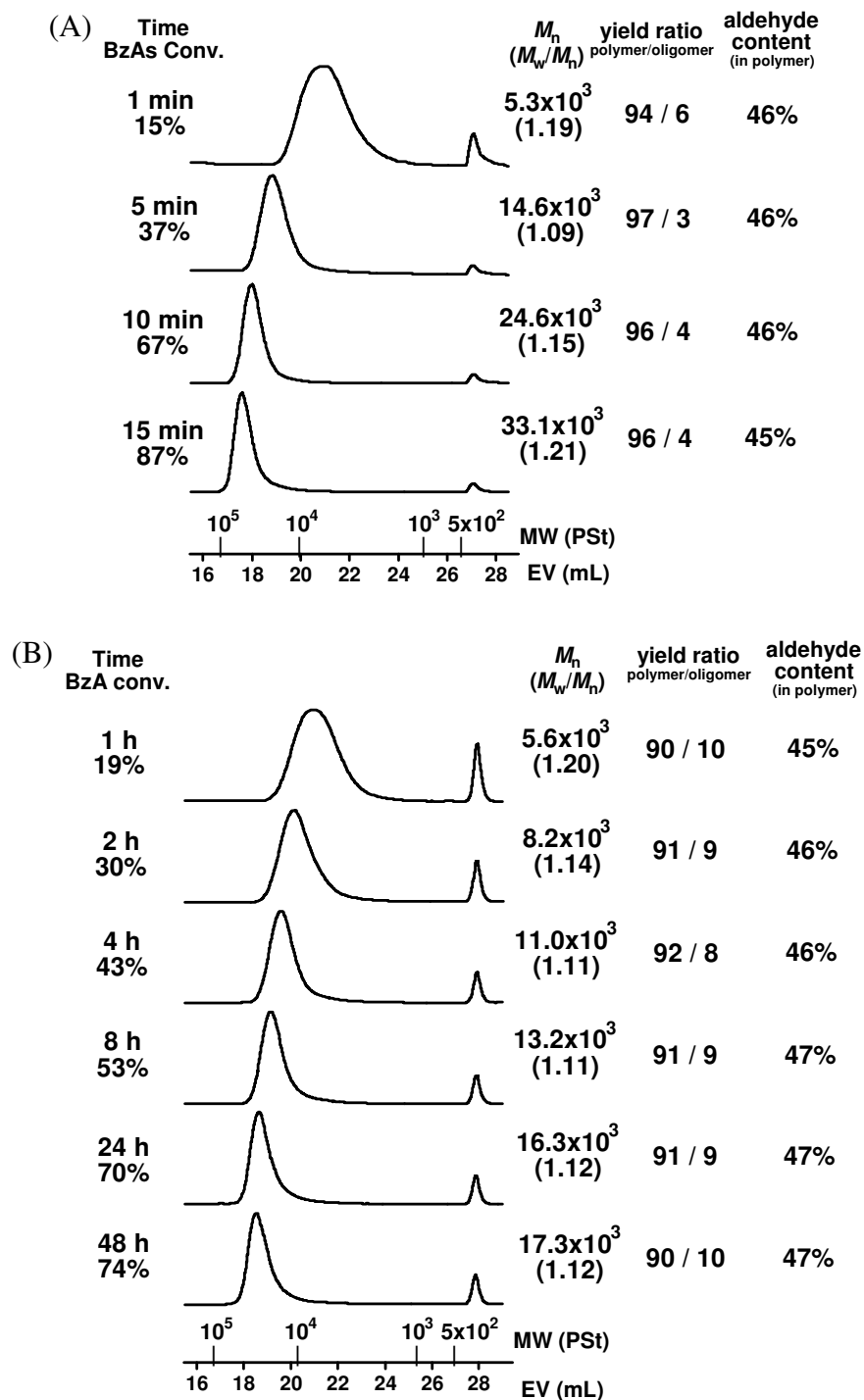


**Figure S4.** Postulated mechanism of acid hydrolysis of nearly alternating poly(benzaldehydes-*co*-vinyl ethers).



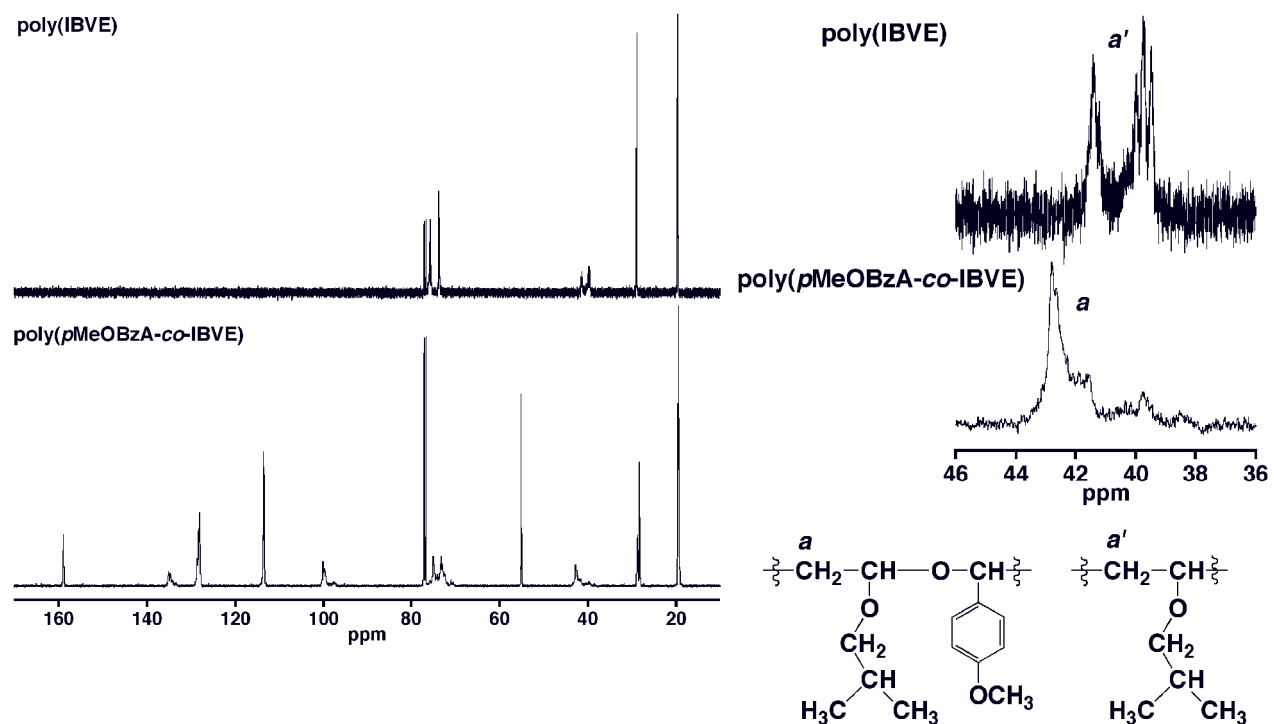
**Figure S5.** Calibration curves for figure 1(B).





**Figure S6.** (A) Molecular weight distribution (MWD) curves of products by copolymerization of *p*-methoxybenzaldehyde (*p*MeOBzA) with isobutyl vinyl ether (IBVE)<sup>a</sup>, and (B) MWD curves of Products by copolymerization of BzA with 2-chloroethyl vinyl ether (CEVE)<sup>b</sup> (All  $M_n$ s and  $M_w/M_n$ s are for main peaks.) (Polymerization conditions: <sup>a</sup>[*p*MeOBzA]<sub>0</sub> = 0.8 M, [IBVE]<sub>0</sub> = 2.0 M, [EtSO<sub>3</sub>H]<sub>0</sub> = 4.0 mM, [GaCl<sub>3</sub>]<sub>0</sub> = 4.0 mM, [1,4-dioxane] = 1.0 M, [2,6-di-*tert*-butylpyridine (DTBP)] = 2.0 mM, in toluene at -78 °C; <sup>b</sup>[BzA]<sub>0</sub> = 0.6 M, [CEVE]<sub>0</sub> = 0.6 M, [EtSO<sub>3</sub>H]<sub>0</sub> = 4.0 mM, [GaCl<sub>3</sub>]<sub>0</sub> = 4.0 mM, [1,4-dioxane] =

1.0 M, in toluene at -78 °C: “BzAconv.” or “BzAs conv.” means aldehyde conversion into Polymer.). [Slight tailings were observed in the GPC profiles. These tailings shifted toward higher molecular weight region with progress of polymerization. Thus, the tailings would not be due to side reaction such as transfer reaction but uneven initiation reaction. The initiation reaction is not perfectly concurrent, leading to a tailing.]



**Figure S7.**  $^{13}\text{C}$  NMR spectra of poly(*p*-methoxybenzaldehyde-co-isobutyl vinyl ether) and poly(isobutyl vinyl ether).