Electronic Supplementary Information

Chemically recyclable alternating copolymers with low polydispersity from conjugated/aromatic aldehydes with vinyl ethers: selective degradation to another monomer at ambient temperature

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Contents:

Experimental Section

Materials. *trans*-Cinnamaldehyde (CinA; Aldrich, 99%) and 2,6-di-*tert*-butylpyridine (DTBP; Aldrich, ≥97.0%) were distilled over calcium hydride twice under reduced pressure before use. (*E*,*E*)-5-Phenylpenta-(2,4)-dienal (PPDE) was synthesized by acid hydrolysis of alternating poly(CinA-*co*-IBVE) and distilled over calcium hydride twice under reduced pressure before use. Isobutyl vinyl ether (IBVE; TCI, >99.0%) was distilled twice over calcium hydride. 1,4-Dioxane (Wako, >99.5%) was distilled over calcium hydride and then lithium aluminum hydride. $EtSO_3H$ (Aldrich, 95%) was used as received. Toluene (Wako, >99.5%) was dried using solvent purification columns (Glass Contour). Dichloromethane (DCM) was distilled twice over calcium hydride (for the reagent from Nacalai, 99%) or dried using solvent purification columns (Glass Contour) (for the reagent from Wako, 99.0%). For $GaCl_3$, a stock solution in hexane was prepared from anhydrous $GaCl_3$ (Aldrich, >99.999%). Hydrochloric acid (Nacalai Tesque) and tetrahydrofuran (THF; Wako, >99.5%) were used as received. All reagents except for toluene, DCM, 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 glass tube equipped with a three-way stopcock. The tube was carefully dried using a heat gun (Ishizaki; PJ-206A; blow temperature ~450 °C) under dry nitrogen before polymerization reactions. A prechilled initiator solution (0.40 mL) was added to a prechilled mixture solution of a monomer, an added base, and a solvent (3.20 mL) at 0 °C by a dry medical syringe. The polymerization reaction was started by the addition of a prechilled Lewis acid solution (0.40 mL) to the prechilled mixture (3.60 mL) at a certain polymerization temperature. The reaction mixture was stirred with a magnetic stir bar throughout the polymerization. The polymerization was quenched with prechilled methanol containing a small amount of aqueous ammonia solution (2.50 mL; 0.1%). The quenched reaction mixture was diluted with DCM and then washed with water to remove the catalyst residues. The volatiles were evaporated under reduced pressure and the residue was vacuum-dried for at least 6 h at 60 °C. The monomer conversion was determined by the gravimetric method and/or ^{1}H NMR analysis

Acid Hydrolysis. Obtained copolymers were purified by reprecipitation in alcohols at least twice to remove low MW oligomers. The purified copolymer (30 mg) was dissolved in THF (5.0 mL), then the reaction was started by the addition of an aqueous HCl-THF (1.0 M; 5.0 mL) solution at 30 °C. The reaction mixture was stirred with a magnetic stir bar throughout the hydrolysis. The hydrolysis was quenched with aqueous sodium hydroxide (1.0 M). The quenched reaction mixture was diluted with DCM, washed with water to remove the resulting salt and evaporated under reduced pressure. The residue was vacuum-dried at room temperature.

Characterization. The 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_{XL}, G-3000H_{XL}, and G-2000H_{XL}; 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; $577–1.09 \times 10^6$ or $292–1.09 \times 10^6$, $M_w/M_n \leq 1.1$). NMR spectra were recorded at 30 °C in $CDCl_3$ or CD_2Cl_2 using a Varian Mercury 300 spectrometer (300 MHz for ^{1}H), a JEOL JNM-LA 500 spectrometer (500 MHz for ^{1}H), or a JEOL ECA 500 spectrometer (500 MHz for ^{1}H). Differential Scanning Calorimetry (DSC EXSTER-6000, Seiko Instruments Inc.) was used to determine the glass transition temperature (T_g) of product copolymers. The heating and cooling rates were 10 °C/min. The T_g of the copolymers was defined as the temperature of the midpoint of a heat capacity change on the second heating scan. Thermogravimetric analysis was performed under nitrogen atmosphere at a heating rate of 10 °C/min using EXSTAR 6000 TG/DTA 6200 (Seiko Instruments, Inc.)

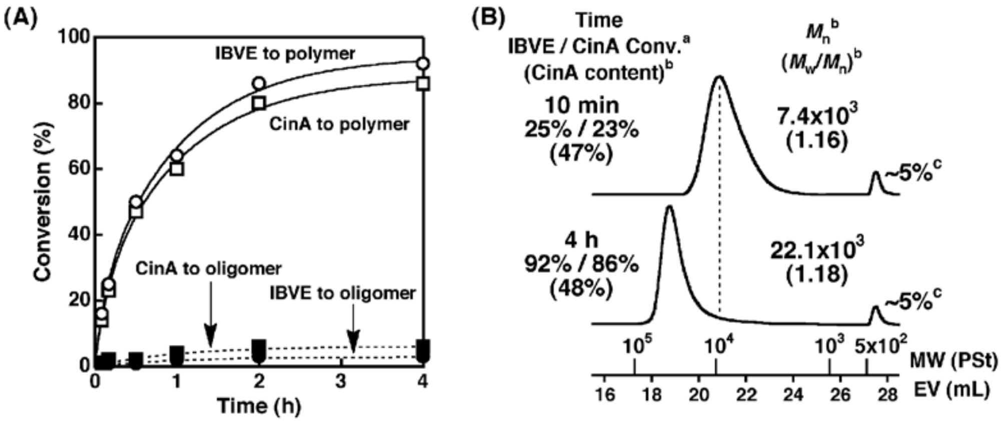

Figure S1. (A) Conversion vs. time curves and (B) MWD curves of products obtained by copolymerization of CinA with IBVE ($[CinA]_0$ = 0.60 M, $[IBVE]_0$ = 0.60 M, $[EtSO_3H]_0$ = 4.0 mM, $[GaCl_3]_0$ = 4.0 mM, [1,4-dioxane] = 1.0 M, in toluene at –78 °C). [a] For polymerization. [b] For polymer. [c] Cyclic trimer ratio in products.

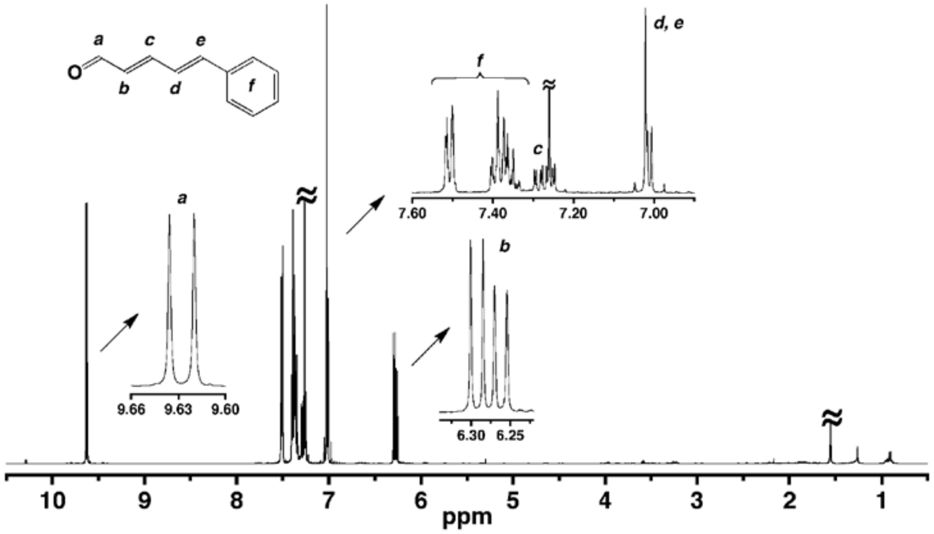

Figure S2. ^{1}H NMR spectrum of the hydrolysis products of poly(CinA-*co*-IBVE) (500.16 MHz in $CDCl_3$ at 30 °C).

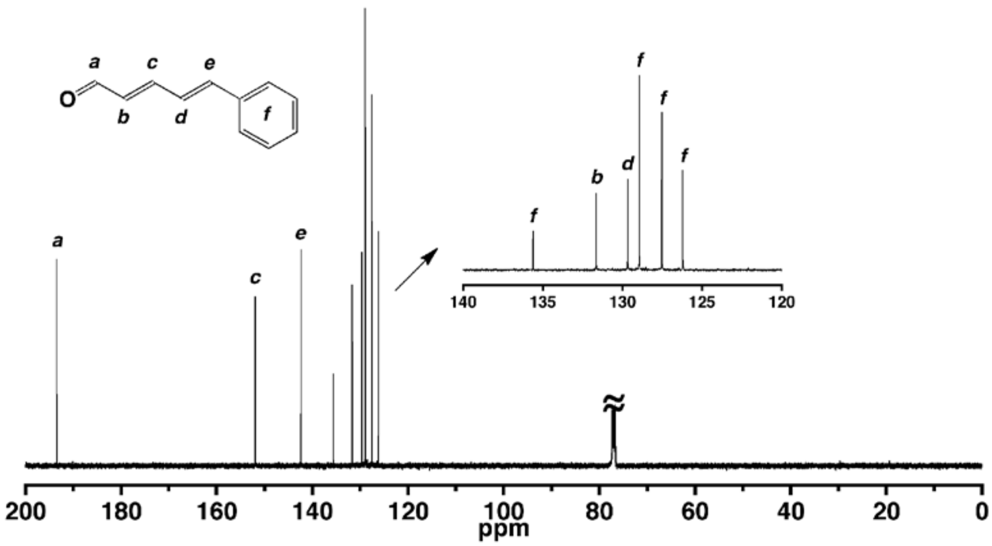

Figure S3. ^{13}C NMR spectrum of the hydrolysis products of poly(CinA-*co*-IBVE) (125.77 MHz in $CDCl_3$ at 30 °C).

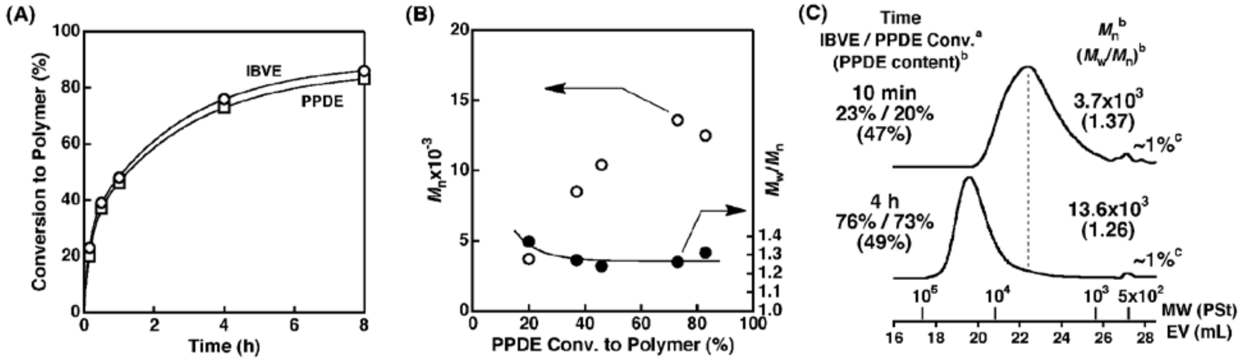

Figure S4. (A) Conversion vs. time curves, (B) M_n and M_w/M_n for polymer peaks, and (C) MWD curves of products obtained by copolymerization of PPDE and IBVE in the absence of DTBP ($[PPDE]_0$ = 0.45 M, $[IBVE]_0$ = 0.45 M, $[EtSO_3H]_0$ = 4.0 mM, $[GaCl_3]_0$ = 4.0 mM, [1,4-dioxane] = 1.0 M, in toluene at –78 °C). ^{a} For polymerization. ^{b} For polymer. ^{c} Cyclic trimer ratio in products.

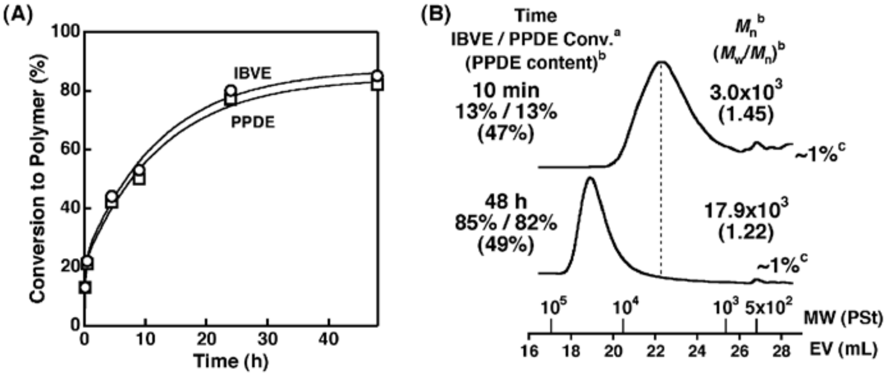

Figure S5. (A) Conversion vs. time curves and (B) MWD curves of products obtained by copolymerization of PPDE and IBVE in the presence of DTBP ($[\mathrm{PPDE}]_0$ = 0.45 M, $[\mathrm{IBVE}]_0$ = 0.45 M, $[\mathrm{EtSO_3H}]_0$ = 4.0 mM, $[\mathrm{GaCl_3}]_0$ = 4.0 mM, [1,4-dioxane] = 1.0 M, [DTBP] = 4.0 mM, in toluene at –78 °C). ^{a} For polymerization. ^{b} For polymer. ^{c} Cyclic trimer ratio in products.

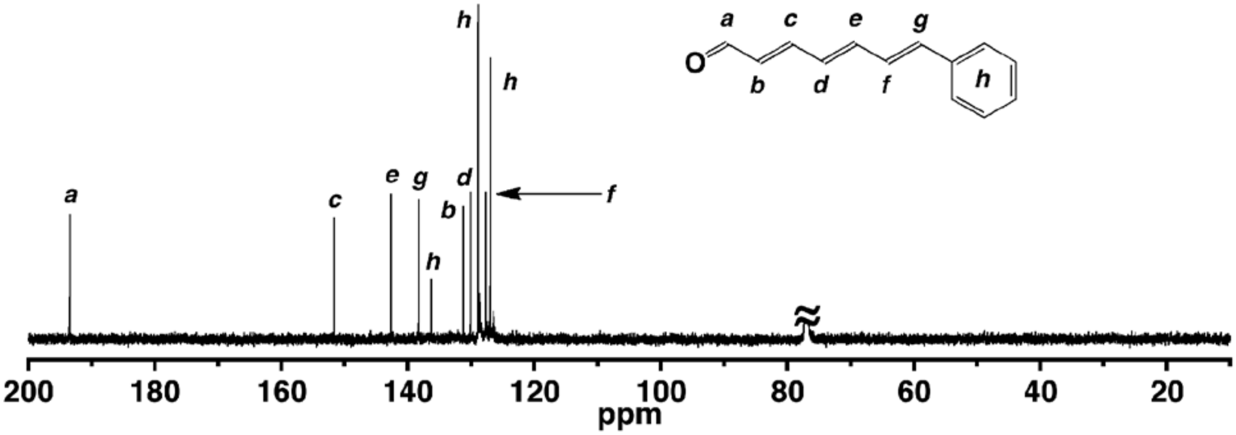

Figure S6. ^{13}C NMR spectrum of the hydrolysis products of poly(PPDE-*co*-IBVE) (125.77 MHz in $\mathrm{CDCl_3}$ at 30 °C).

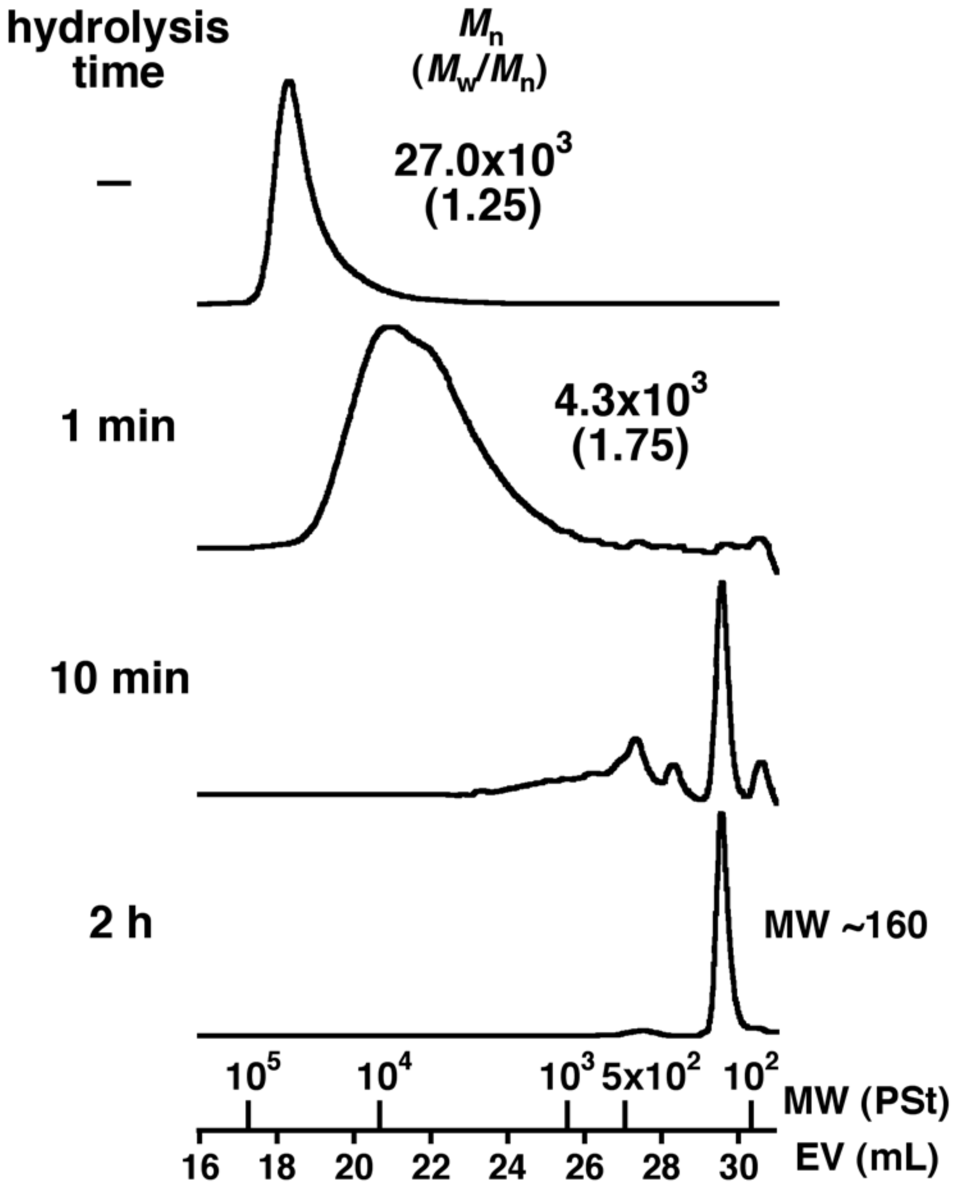

Figure S7. MWD curves of original polymers and hydrolysis products for poly(*p*-methoxyBzA-*co*-IBVE) [M_n(GPC) = 2.70 × 10^4, M_w/M_n(GPC) = 1.25, *p*MeOBzA content: 45%] (hydrolysis conditions: 0.50 M aqueous HCl-THF at 30 °C).