Electronic Supplementary Information

Polymerization and Degradation of Aliphatic Polyesters Synthesized by Atom Transfer Radical Polyaddition

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Captions of ESI

Experiments

Synthesis of VBBiB. As displayed in Scheme S1, 4-vinylbenzyl alcohol (VBA) was synthesized from VBC using a previously reported procedure[1] (yield 94%; ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 4.64 (s, PhCH_2, 2H), 5.25, 5.76 (d, CH_2=CH, 2H), 6.68–6.75 (dd, CH_2=CH, 1H), 7.29–7.41 (m, C_6H_4, 4H)). For the synthesis of VBBiB, a dry 500-mL two-neck round-bottom flask was charged with VBA (24 g, 180 mmol) and triethylamine (40 mL, 290 mmol) via syringes and mixed well in dry CH_2Cl_2 (300 mL) under N_2. A solution of 2-bromoisobutyryl bromide (8.5 g, 290 mmol) was added dropwise to the mixture over a period of a few hours with stirring at 0 °C. The mixture was warmed to room temperature and the reaction continued for an additional 24 h under N_2. The solids were filtered off; the filtrate washed with 1 M $HCl_{(aq)}$, 1 M $NaOH_{(aq)}$, and water and then dried ($MgSO_4$). After evaporation of the solvents, the residue was purified through a column of silica (EtOAc/hexane, 1:20 (v/v)) to give a light-yellowish liquid (yield 96%; ^{1}H NMR (400 MHz, $CDCl_3$, δ = ppm): 1.95 (s, C(CH_3)$_2$Br, 6H), 5.19 (s, PhCH_2, 2H), 5.27, 5.77 (d, CH_2=CH, 2H), 6.68–6.75 (dd, CH_2=CH, 1H), 7.33–7.43 (m, C_6H_4, 4H)). ^{1}H NMR and FT-IR spectra are presented in Figure S1.

Synthesis of PVBAiB. A 10-mL round-bottom flask was charged with PVBCiB (0.20 g, 0.034 mmol), NaN_3 (0.50 g, 7.6 mmol), and DMF (10 mL). The reaction mixture was stirred at –20 °C for 48 h and then diluted with CH_2Cl_2 and washed three times with water. The solution was concentrated under vacuum and the polymer precipitated in water twice. The polymers were dried in a vacuum oven at 40 °C for 24 h (yield: 40%). ^{1}H NMR and FT-IR spectra are displayed in Figure S5.

Scheme S1. Syntheses of the model compounds BzBDT and BzCDT.

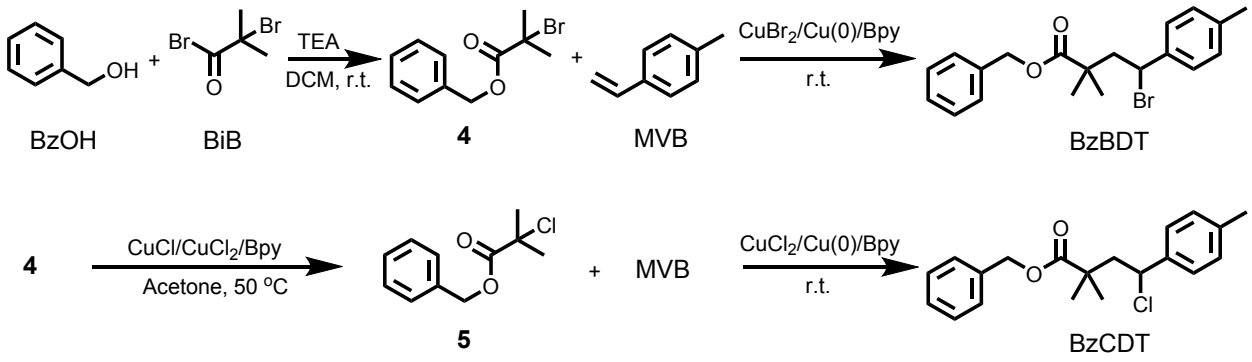


Figure S1. (A) ^{1}H NMR (400 MHz, $CDCl_3$) and (B) FT-IR spectra of VBBiB.

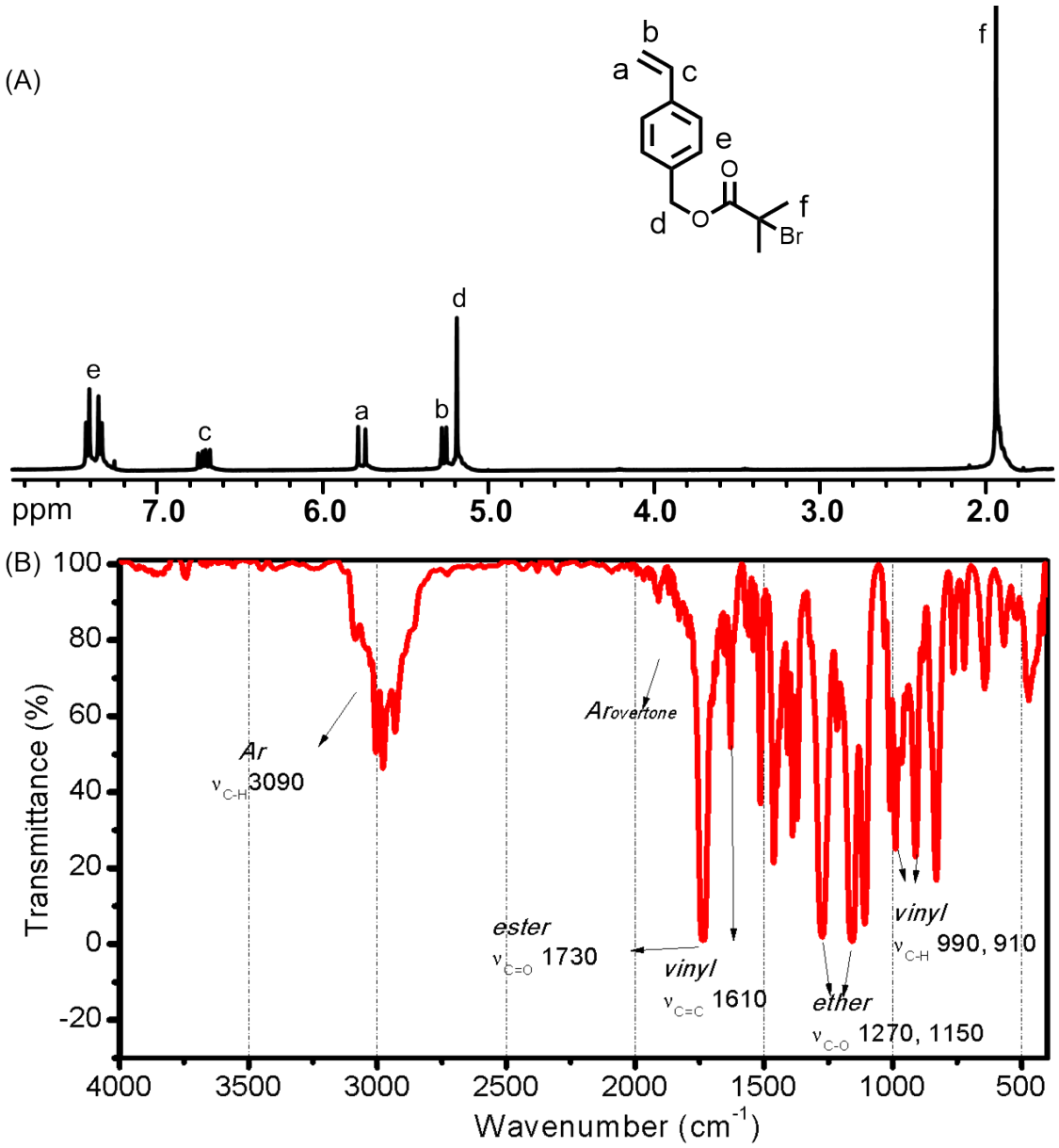


Figure S2. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **4**, **5**, BzBDT and BzCDT.

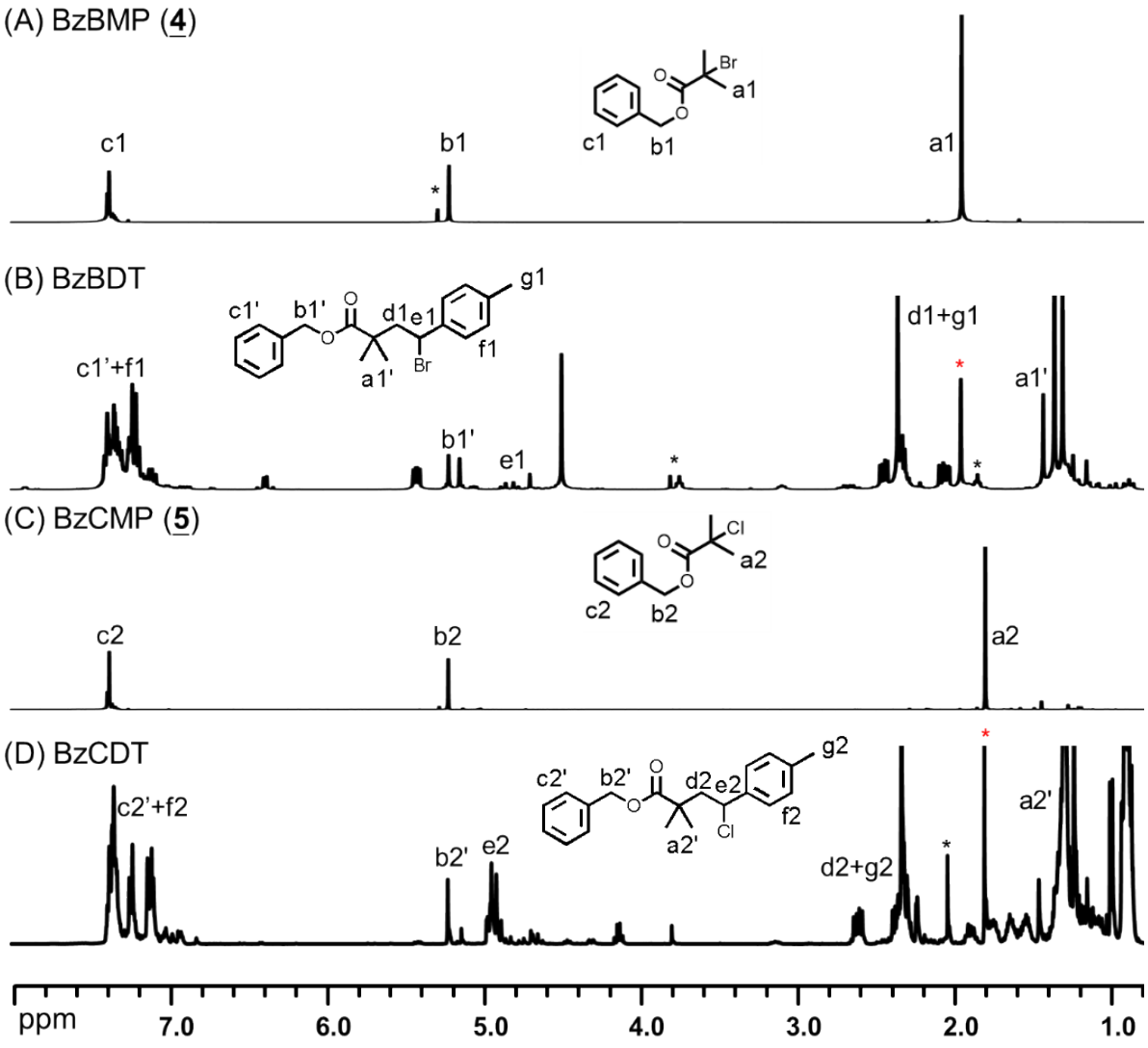


Figure S3. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of the model compound BzCDT after 0, 7, and 24 days.

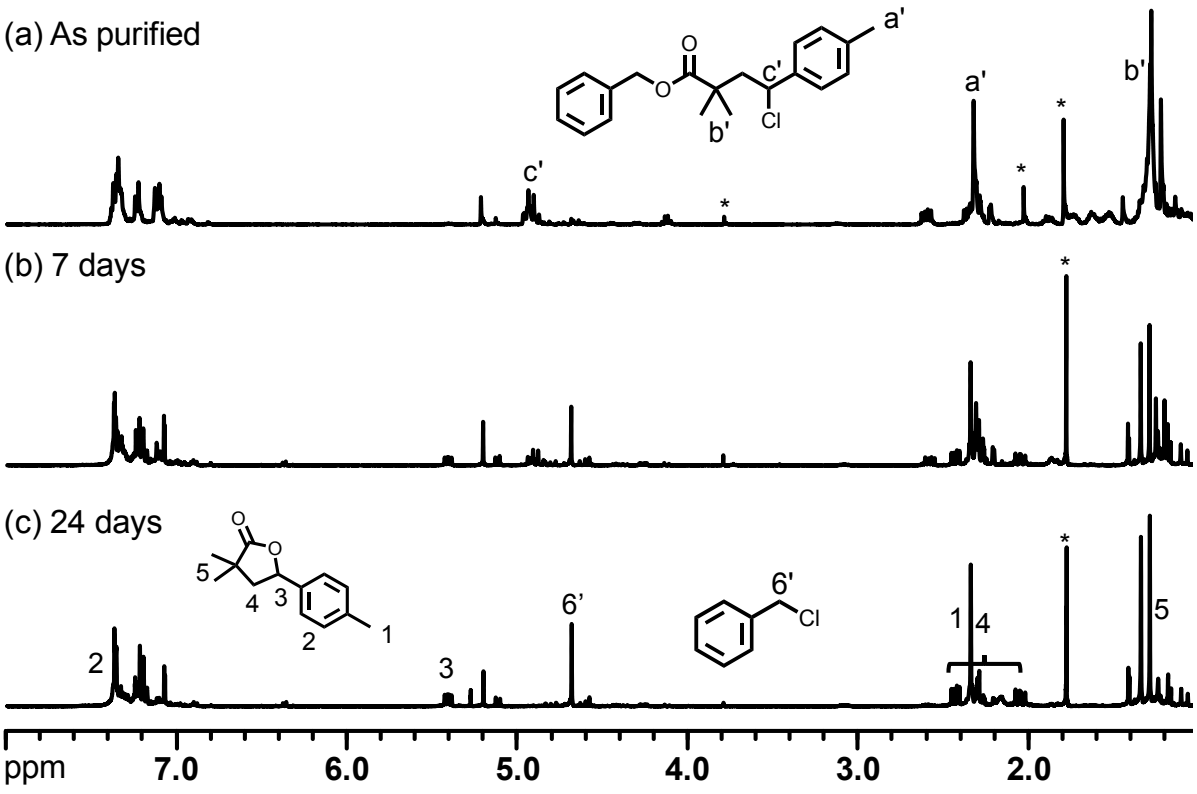


Figure S4. (A) ^{1}H NMR (400 MHz, $CDCl_3$) and (B) FT-IR spectra of PVBAiB.

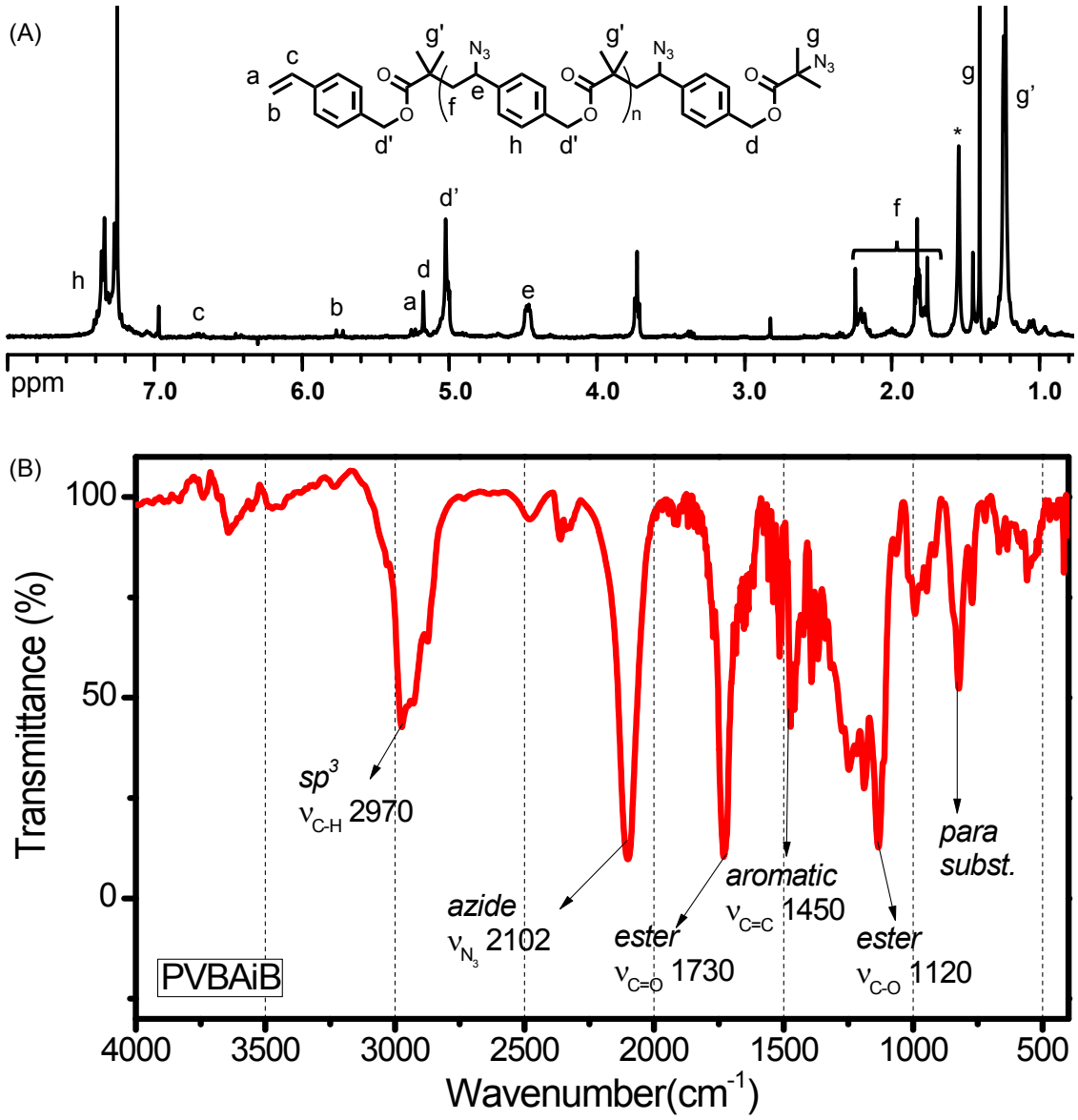
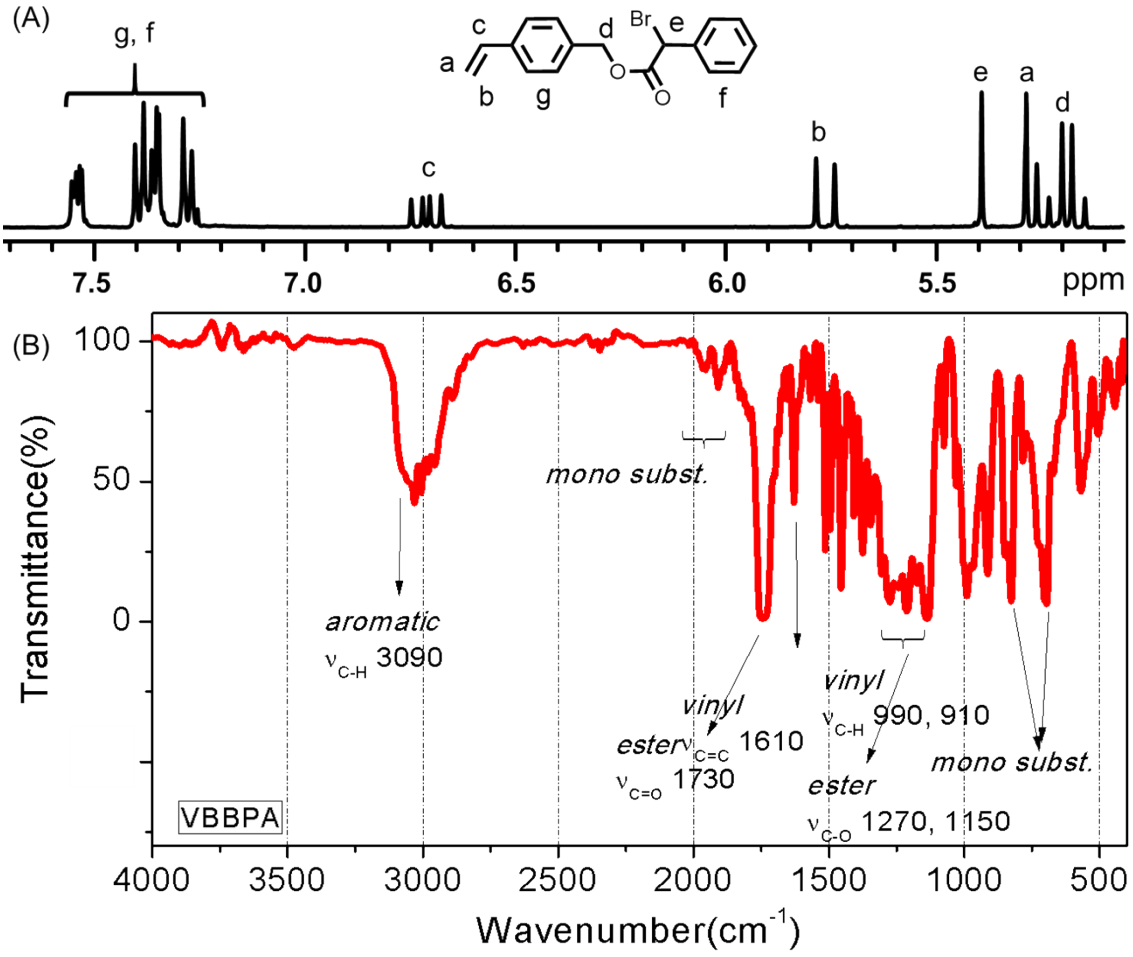


Figure S5. (A) ^{1}H NMR (400 MHz, $CDCl_3$) and (B) FT-IR spectra of VBBPA.



Reference

1. J. O. Park and S. H. Jang, *J Polym Sci Pol Chem*, 1992, **30**, 723-729.