Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary information for

Synthesis of performance-advantaged polyurethanes and polyesters from biomass-derived monomers by aldol-condensation of 5-hydroxymethyl furfural and hydrogenation

Hochan Chang[a], Elise B. Gilcher[a,b], George W. Huber[a], and James A. Dumesic[a,b*]

a. Department of Chemical and Biological Engineering, University of Wisconsin–Madison, Madison, WI, USA.

b. DOE Great Lakes Bioenergy Research Center, University of Wisconsin–Madison, Madison, WI, USA.

*Corresponding author. E-mail: jdumesic@wisc.edu

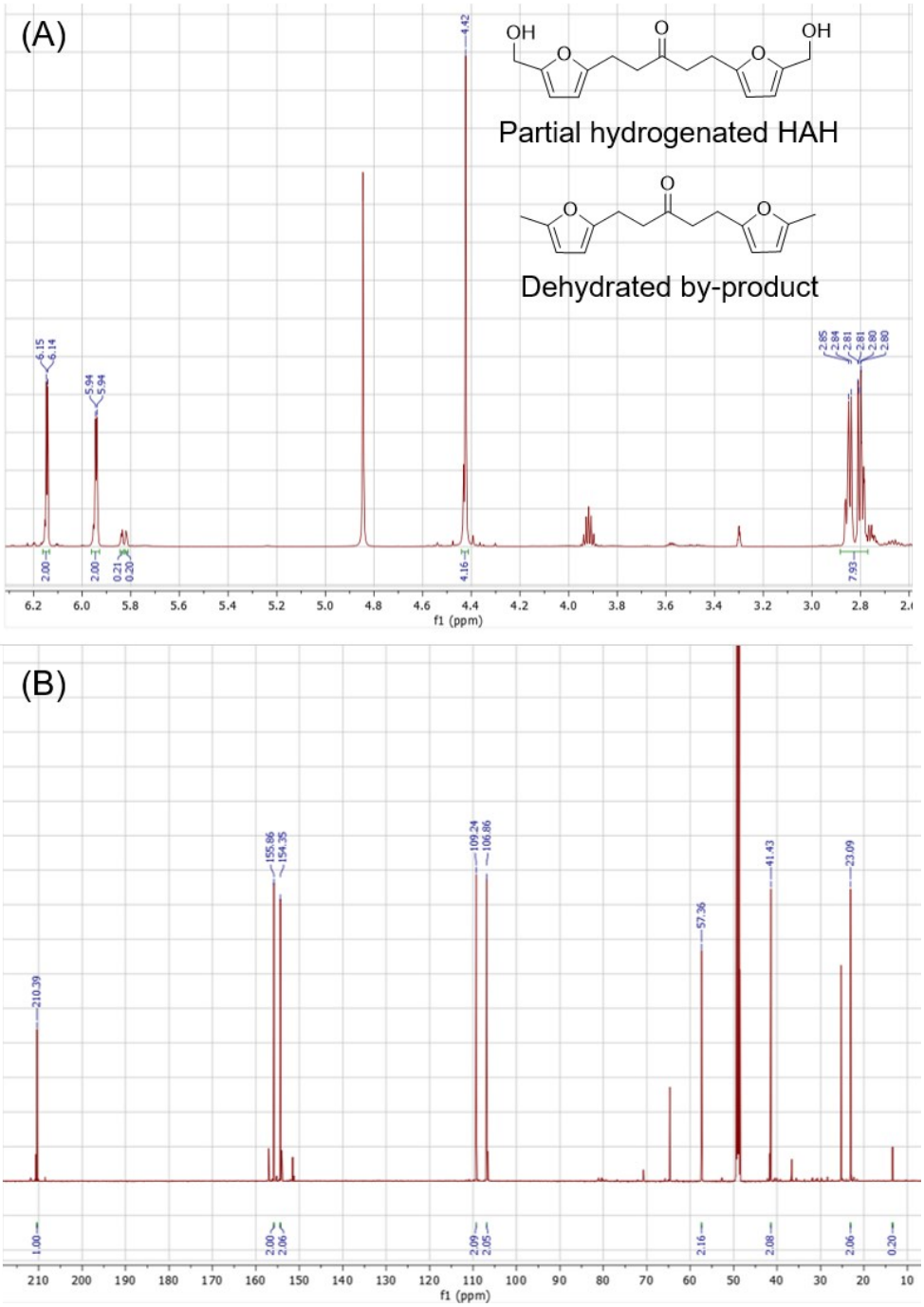

Figure S1. (A) ^{1}H NMR and (B) ^{13}C qNMR of partially hydrogenated HAH (PHAH) from HAH hydrogenation over Cu/γ-Al_2O_3. ^{1}H NMR: (500 MHz, MeOD) δ 6.15 (d, 2H), 5.94 (d, 2H), 4.42 (s, 4H), 2.85-2.80 (m, 8H) ppm, ^{13}C qNMR (126 MHz, MeOD) δ 210.39 (1C), 155.86 (2C), 154.35 (2C), 109.24 (2C), 106.86 (2C), 57.39 (2C), 41.43 (2C), 23.09 (2C) ppm.

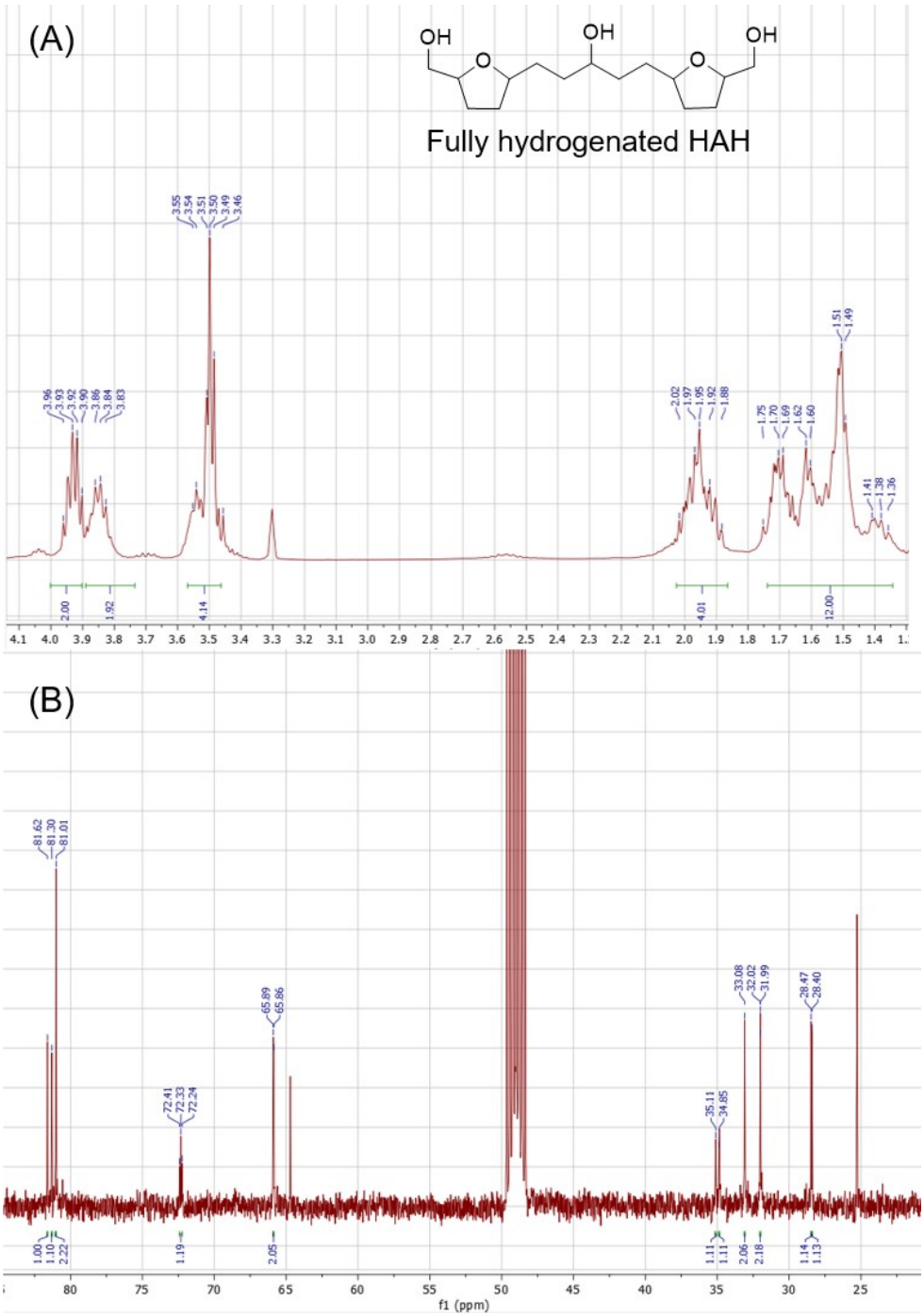

Figure S2. (A) ^{1}H NMR and (B) ^{13}C qNMR of fully hydrogenated HAH (FHAH) from HAH hydrogenation over Ru/C. ^{1}H NMR: (500 MHz, MeOD) δ 3.96-3.90 (m, 2H), 3.90-3.83 (m, 2H), 3.55-3.46 (m, 4H), 2.02-1.88 (m, 4H), 1.75-1.36 (m, 12H) ppm, ^{13}C qNMR (126 MHz, MeOD) δ 81.62 (1C), 81.30 (1C), 81.01 (2C), 72.41-72.24 (1C), 65.89-65.86 (2C), 35.11-34.85 (2C), 33.08 (2C), 32.02-31.99 (2C), 28.47-28.40 (2C) ppm (Splits of ^{13}C chemical shifts resulted from diastereoisomers).

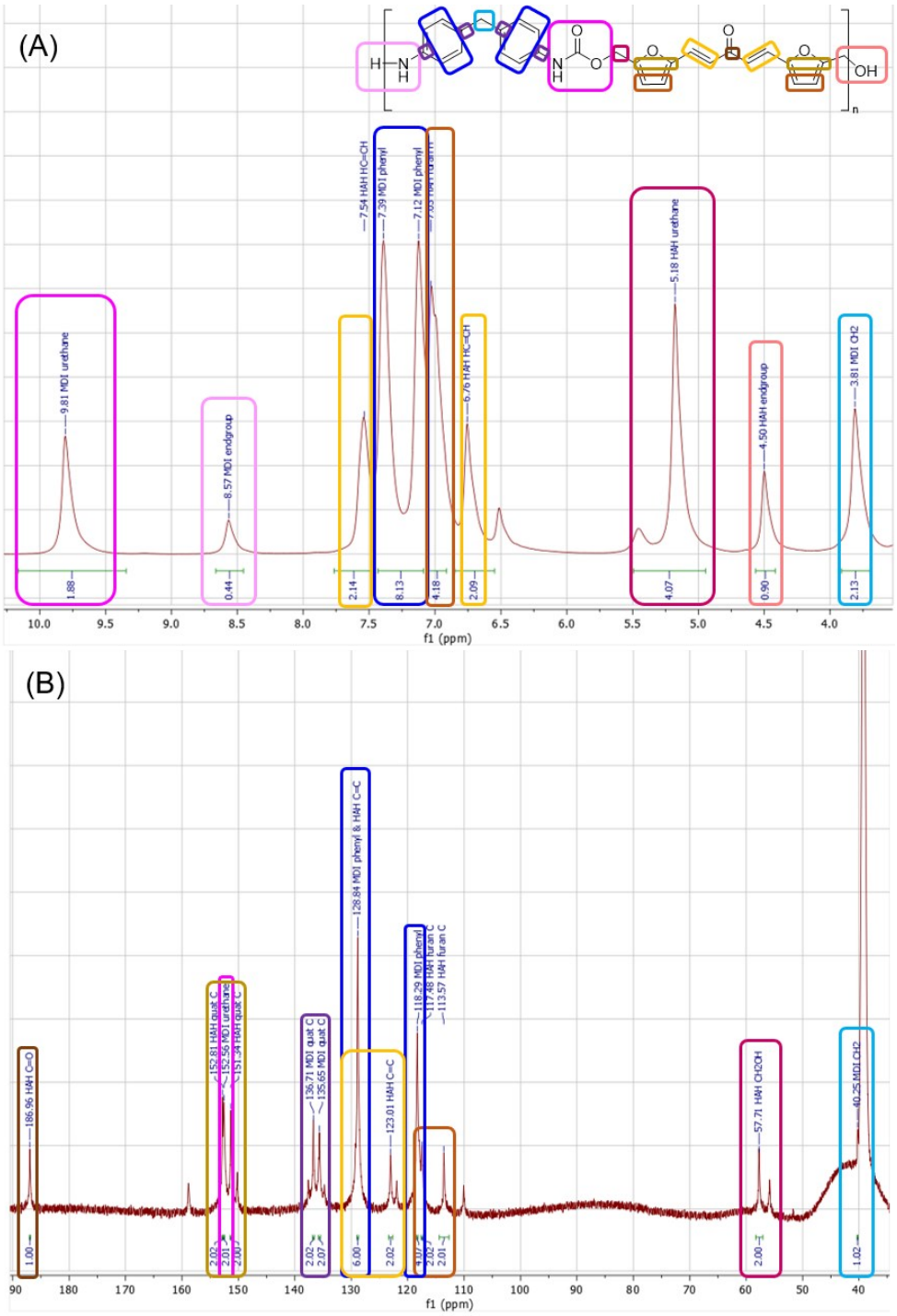

Figure S3. (A) ^{1}H NMR and (B) ^{13}C qNMR of HAH-MDI. ^{1}H NMR: (500 MHz, DMSO-d_6) δ 9.81 (2H), 7.54 (2H), 7.39-7.12 (8H), 7.03 (4H), 6.76 (2H), 5.18 (4H), 3.81 (2H) ppm (CH_2OH group : NHCOO group (mol) = 0.90/2 (4.50 ppm) : 1.88 (9.81 ppm) by ^{1}H NMR; DP=4; Degree of polymerization was defined by ratio of NHCOO group to CH_2OH group), ^{13}C qNMR (126 MHz, DMSO-d_6) δ 186.96 (1C), 152.81 (2C), 152.56 (2C), 151.34 (2C), 136.71 (2C), 135.65 (2C), 128.84 (6C), 123.01 (2C), 118.29 (4C), 117.48 (2C), 113.57 (2C), 57.71 (2C), 40.25 (1C) ppm (HAH unit : MDI unit (mol) = 1 : 1 by ^{13}C qNMR).

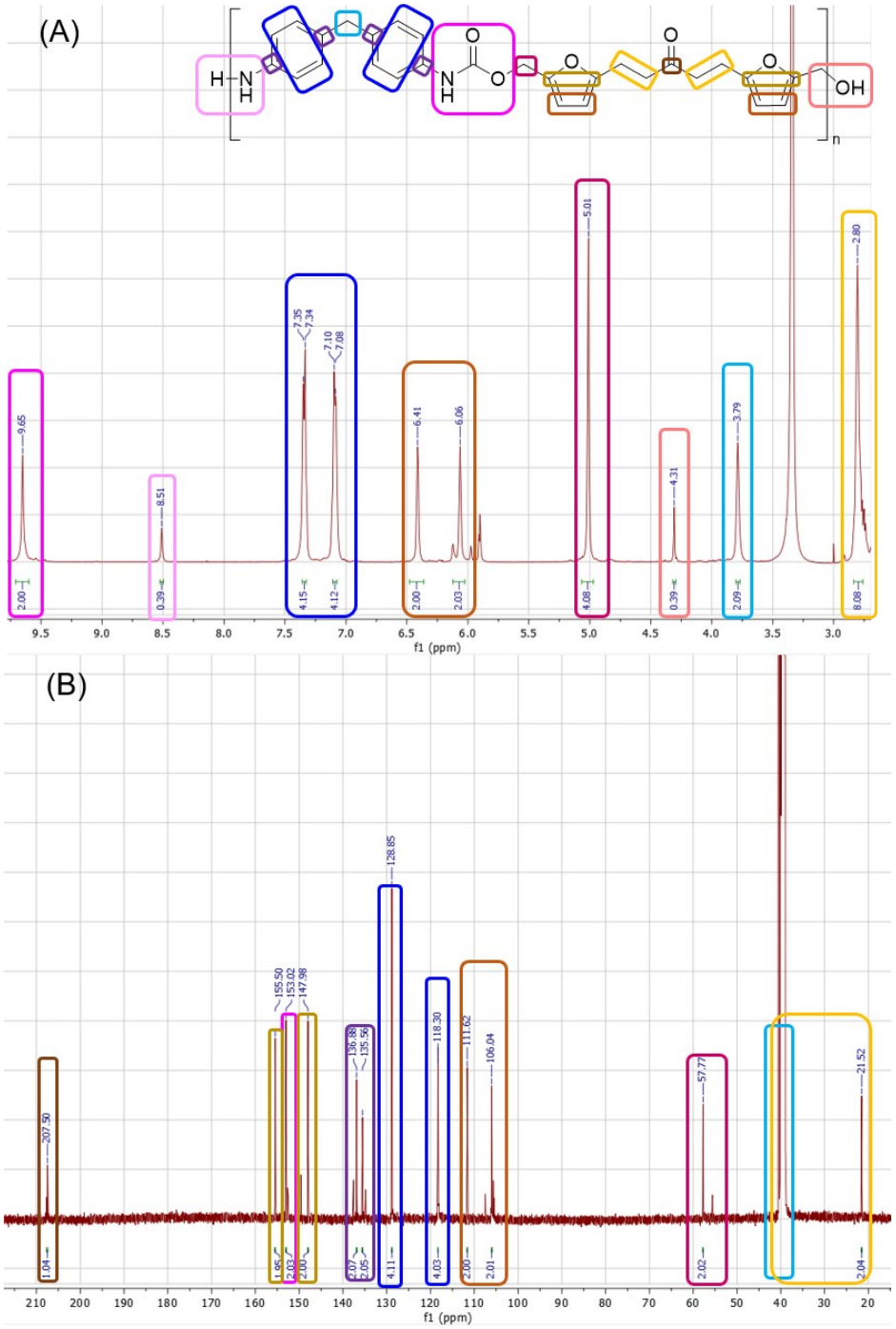

Figure S4. (A) ^{1}H NMR and (B) ^{13}C qNMR of PHAH-MDI. ^{1}H NMR: (500 MHz, DMSO-d_6) δ 9.65 (2H), 7.35-7.34 (4H), 7.10-7.08 (4H), 6.41 (2H), 6.06 (2H), 5.01 (4H), 3.79 (2H), 2.80 (8H) ppm (CH_2OH group : NHCOO group (mol) = 0.39/2 (4.31 ppm) : 2.00 (9.65 ppm) by ^{1}H NMR; DP=10; Degree of polymerization was defined by ratio of NHCOO group to CH_2OH group), ^{13}C qNMR (126 MHz, DMSO-d_6) δ 207.50 (1C), 155.50 (2C), 153.02 (2C), 147.98 (2C), 136.88 (2C), 135.56 (2C), 128.85 (4C), 118.30 (4C), 111.62 (2C), 106.04 (2C), 57.77 (2C), 39.93 (1C), 39.60 (2C), 21.52 (2C) ppm (PHAH unit : MDI unit (mol) = 1 : 1 by ^{13}C qNMR).

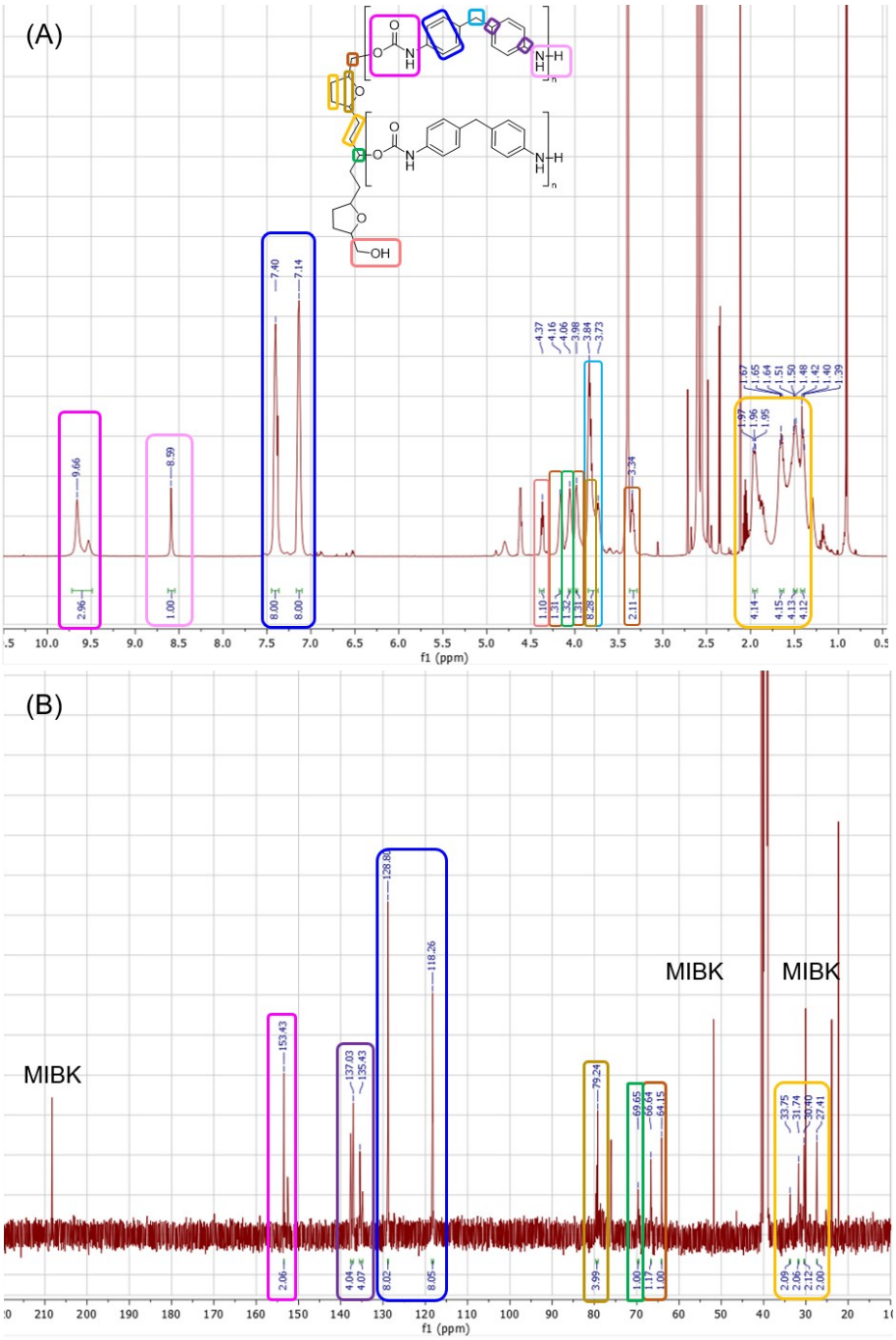

Figure S5. (A) ^{1}H NMR and (B) ^{13}C qNMR of FHAH-MDI. ^{1}H NMR: (500 MHz, DMSO-d_6) δ 9.66-8.59 (4H), 7.40 (8H), 7.14 (8H), 4.16 (1H), 4.06 (1H), 3.98 (1H), 3.84-3.72 (8H), 3.34 (2H), 1.97-1.95 (4H), 1.67-1.64 (4H), 1.51-1.48 (4H), 1.42-1.39 (4H) ppm (CH_2OH group : NHCOO group (mol) = 1.10/2 (4.37 ppm) : 2.96 (9.65 ppm) by ^{1}H NMR; DP=5; Degree of polymerization was defined by ratio of NHCOO group to CH_2OH group), ^{13}C qNMR (126 MHz, DMSO-d_6) δ 153.43 (2C), 137.03 (4C), 135.43 (4C), 128.80 (8C), 118.26 (8C), 79.24 (4C), 69.65 (1C), 66.64 (1C), 64.15 (1C), 33.75 (2C), 31.74 (2C), 30.40 (2C), 27.41 (2C) ppm (FHAH unit : MDI unit (mol) = 1 : 2 by ^{13}C qNMR).

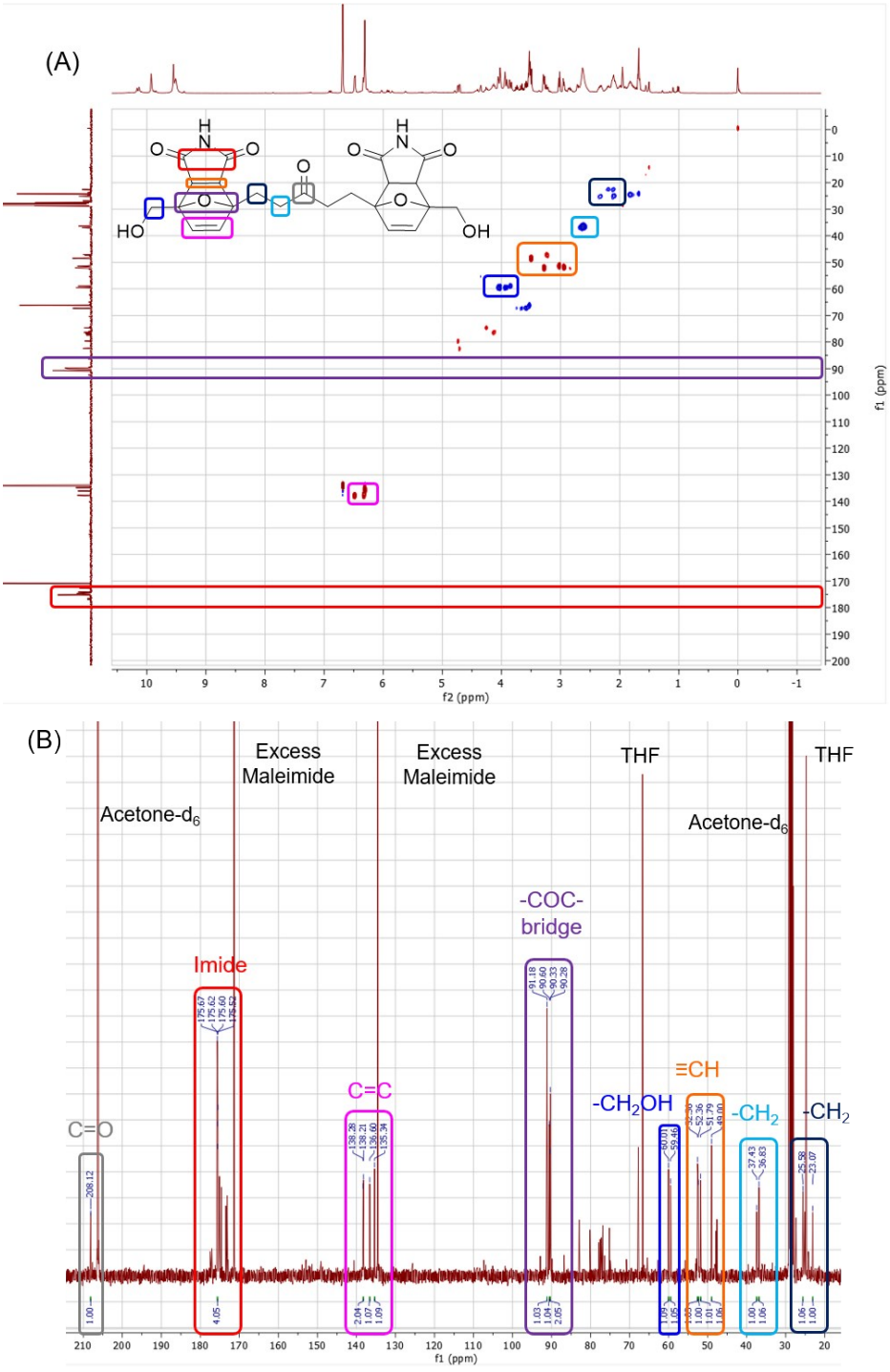

Figure S6. (A) HSQC NMR (Blue dot: CH_2, Red dot: CH_3 or CH) and (B) ^{13}C qNMR of Diels-Alder coupled PHAH and maleimide. ^{13}C qNMR (126 MHz, Acetone-d_6) δ 208.12 (1C), 175.67-175.52 (4C), 138.28-135.37 (4C), 91.18-90.28 (4C), 60.01-59.46 (2C), 52.36-49.00 (4C), 37.43-36.83 (2C), 25.58-23.07 (2C) ppm (Splits of ^{13}C chemical shifts resulted from endo- and exo-diastereoisomers).

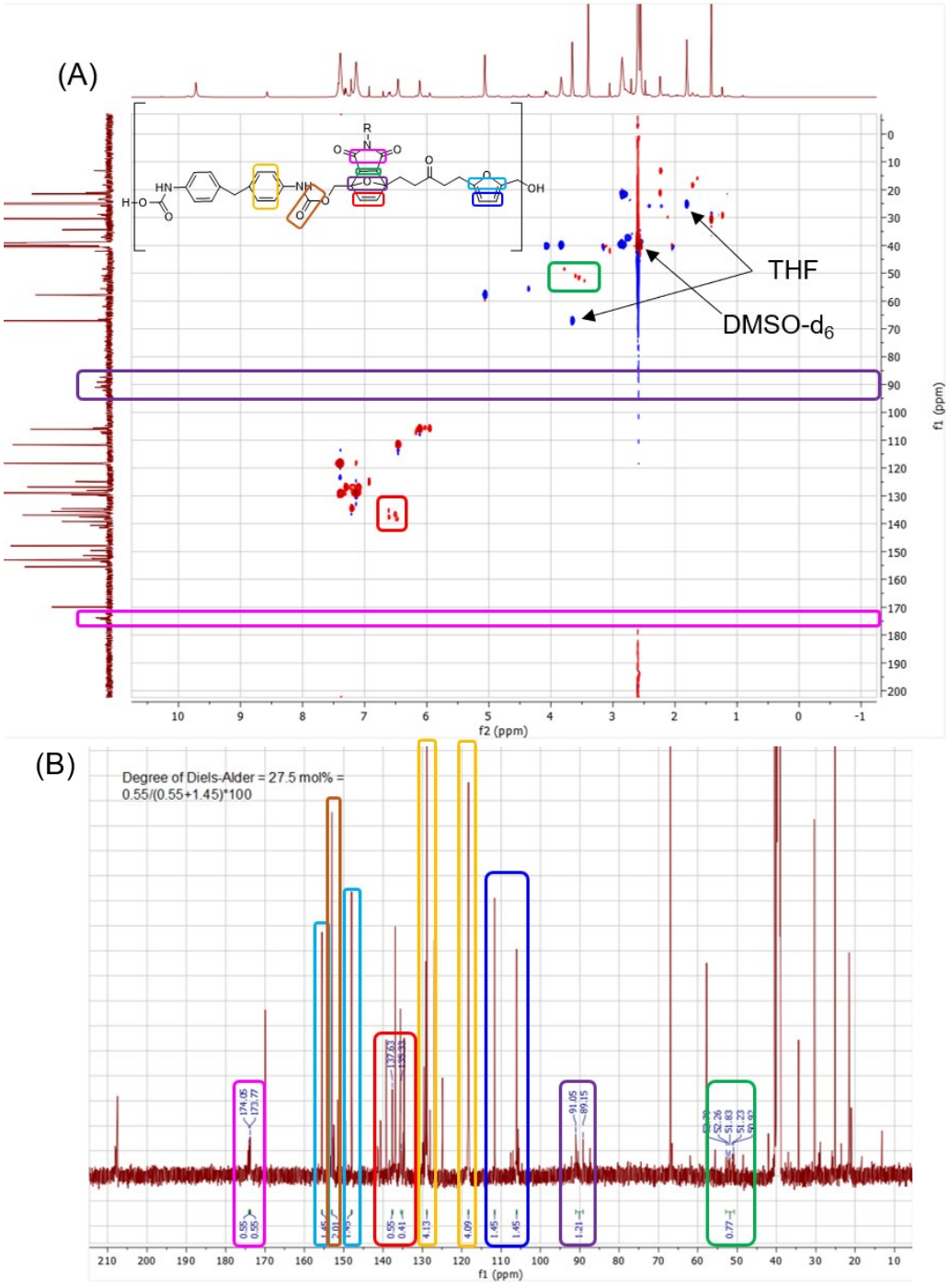

Figure S7. (A) HSQC NMR (Blue dot: CH_2, Red dot: CH_3 or CH) and (B) ^{13}C qNMR of Diels-Alder coupled PHAH-MDI and bismaleimide. ^{13}C qNMR (126 MHz, DMSO-d_6) δ 174.05-173.77 (Diel-Alder coupled imide), 137.63-135.33 (Diel-Alder coupled C=C), 91.05-89.15 (Diel-Alder coupled quaternary COC), 52.79-50.92 (Diel-Alder coupled ≡CH) ppm (Degree of Diels-Alder crosslinking = peak area of Diels-Alder coupled

bismaleimide unit/(peak area of Diels-Alder coupled bismaleimide unit + peak area of unreacted PHAH unit) = 27.5 mol%).

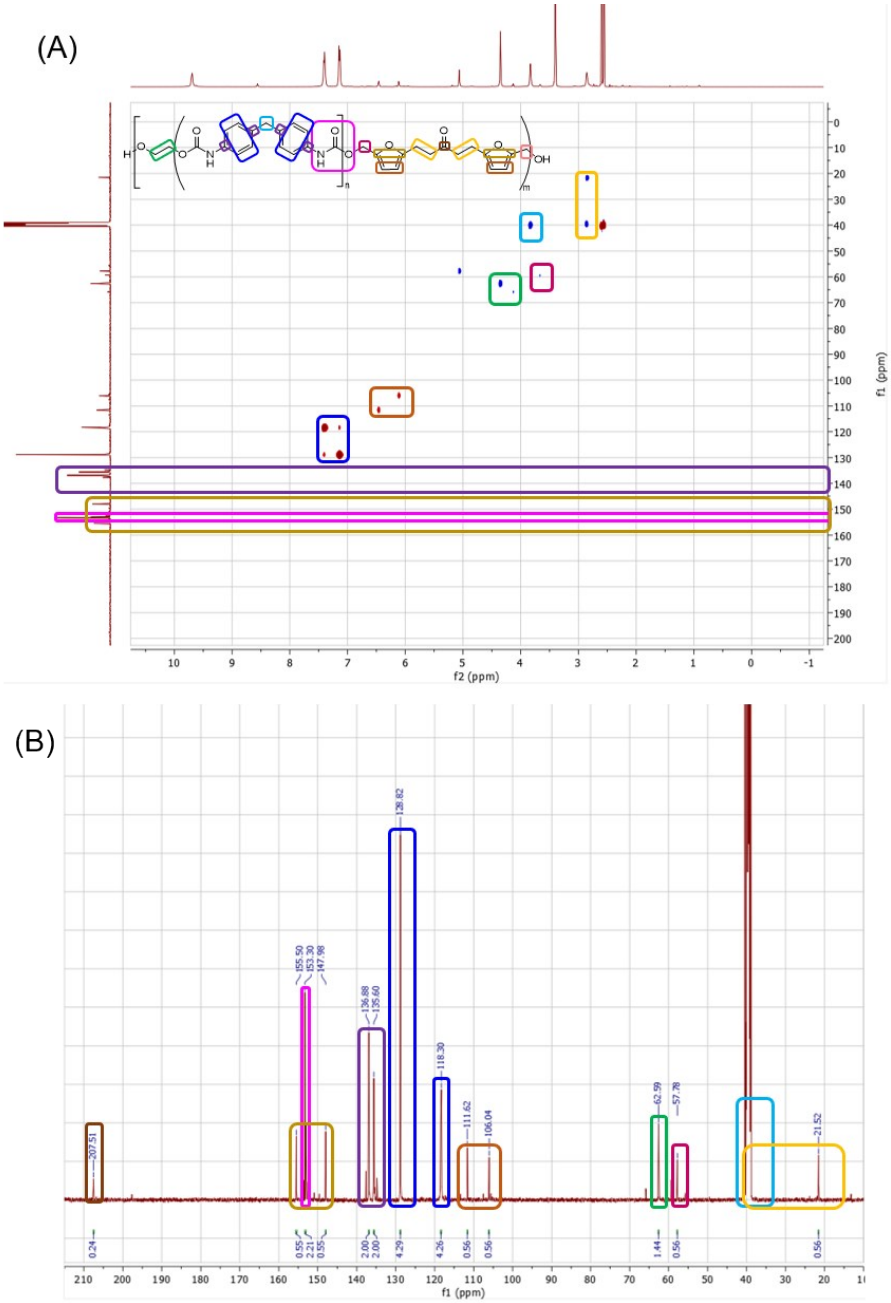

Figure S8. (A) HSQC NMR (Blue dot: CH_2, Red dot: CH_3 or CH) and (B) ^{13}C qNMR of the EG-PHAH-MDI. ^{13}C qNMR (126 MHz, DMSO-d_6) δ 207.51 (0.24C), 155.50 (0.56C), 153.30 (2C), 147.98 (0.55C), 136.88 (2C), 135.60 (2C), 128.82 (4C), 118.30 (4C), 111.62 (0.56C), 106.04 (0.56C), 62.59 (1.44C), 57.79 (0.56C), 39.93 (1C), 39.55 (0.56C), 21.52 (0.56C) ppm (EG unit : PHAH unit : MDI unit = 0.72 : 0.28 : 1.00, EG indicates ethylene glycol).

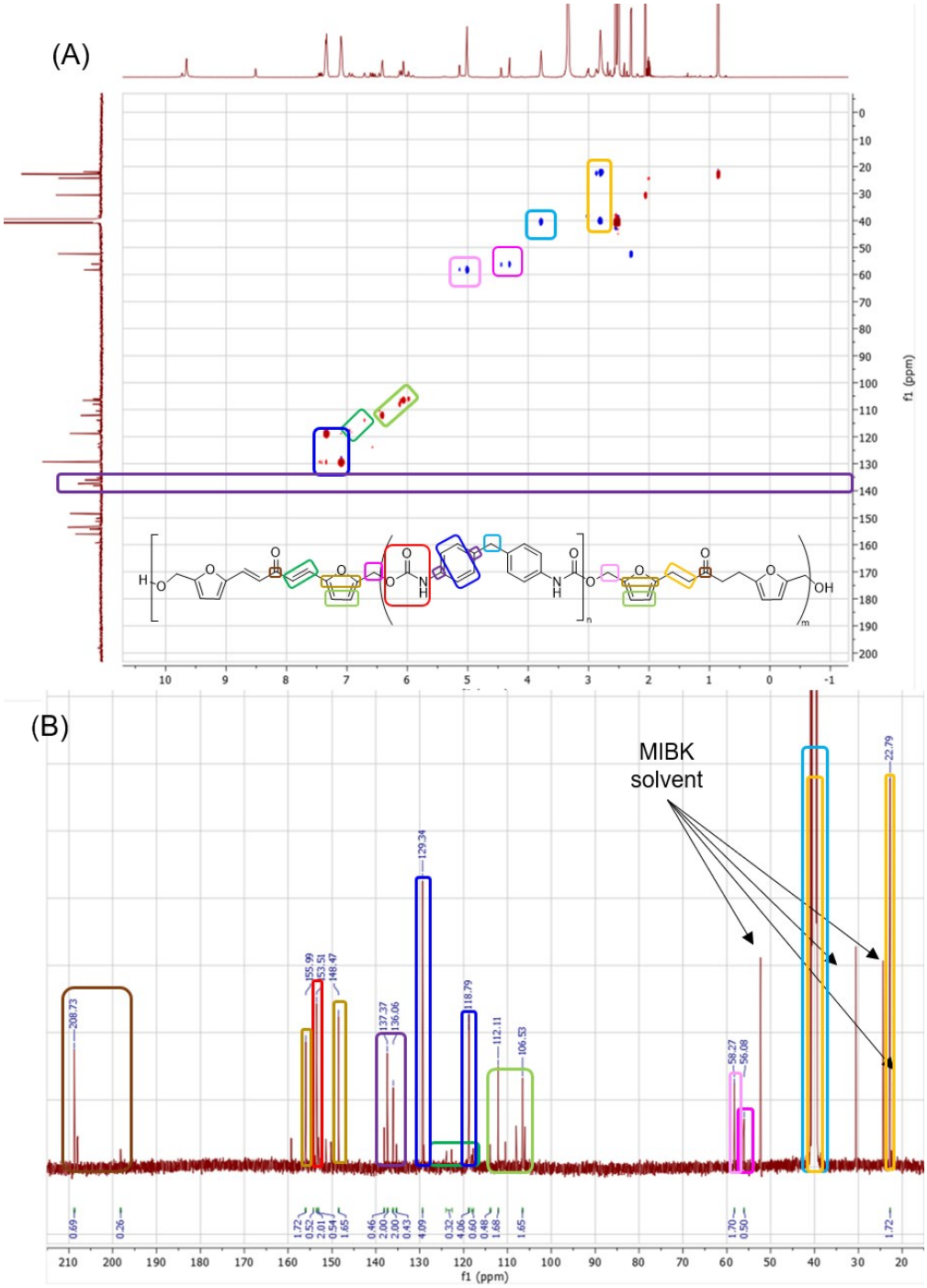

Figure S9. (A) HSQC NMR (Blue dot: CH_2, Red dot: CH_3 or CH) and (B) ^{13}C qNMR of the HAH-PHAH-MDI. ^{13}C qNMR (126 MHz, DMSO-d_6) δ 208.73-198.19 (1C), 155.99 (1.7C), 153.51 (2C), 148.47 (1.7C), 137.37 (2C), 136.06 (2C), 129.34 (4C), 118.79 (4C), 112.11 (1.7C), 106.53 (1.7C), 58.27 (1.7C), 56.08 (0.50C), 40.37 (1C), 40.06 (1.7C), 22.79 (1.7C) ppm (HAH unit : PHAH unit : MDI unit = 0.50 : 1.70 : 2.00).

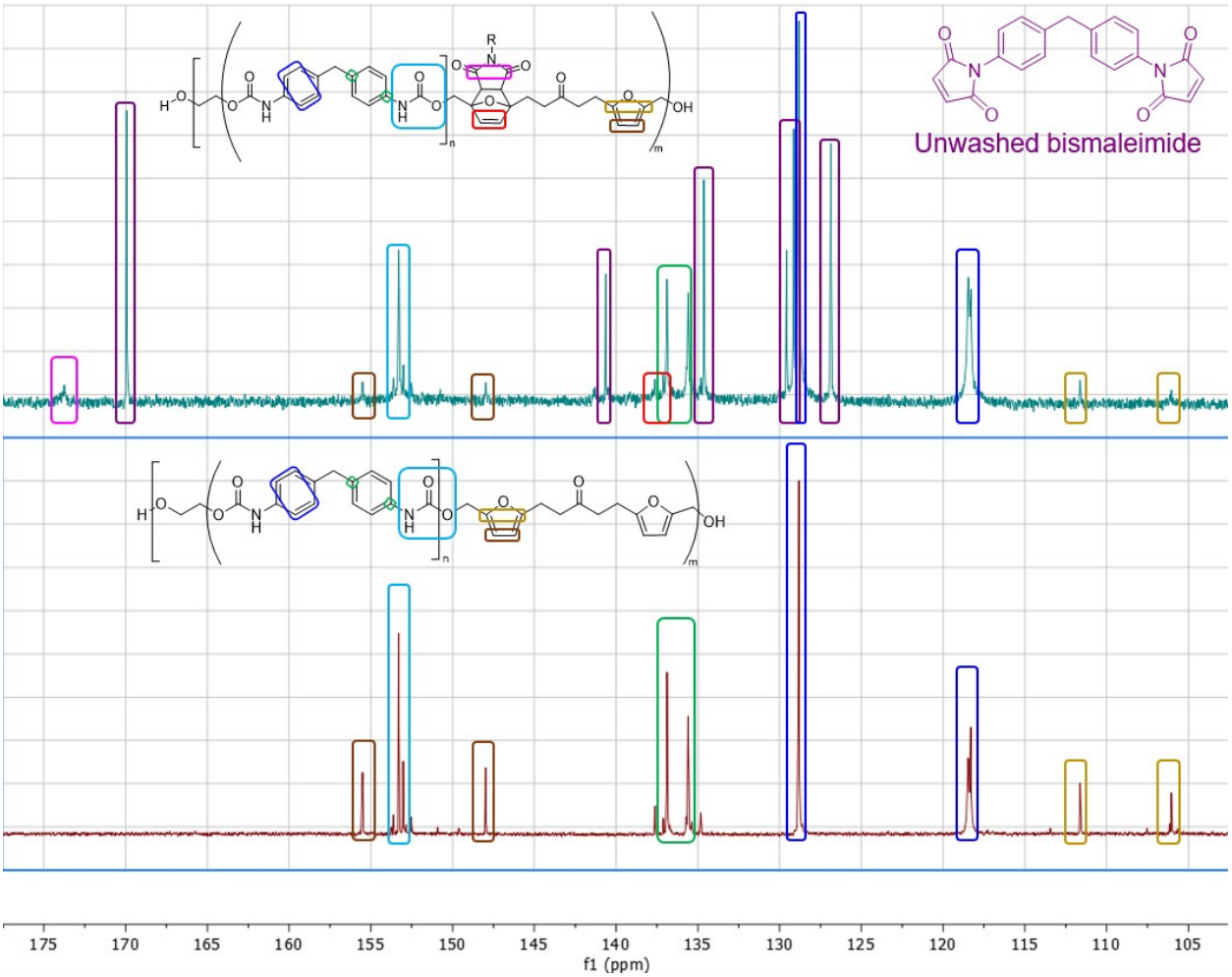

Figure S10. ^{13}C qNMR comparison between EG-PHAH-MDI (bottom) and EG-PHAH-MDI after Diels-Alder crosslinking (top); 48 mol% conversion of bismaleimide was measured by HPLC after Diels-Alder reaction.

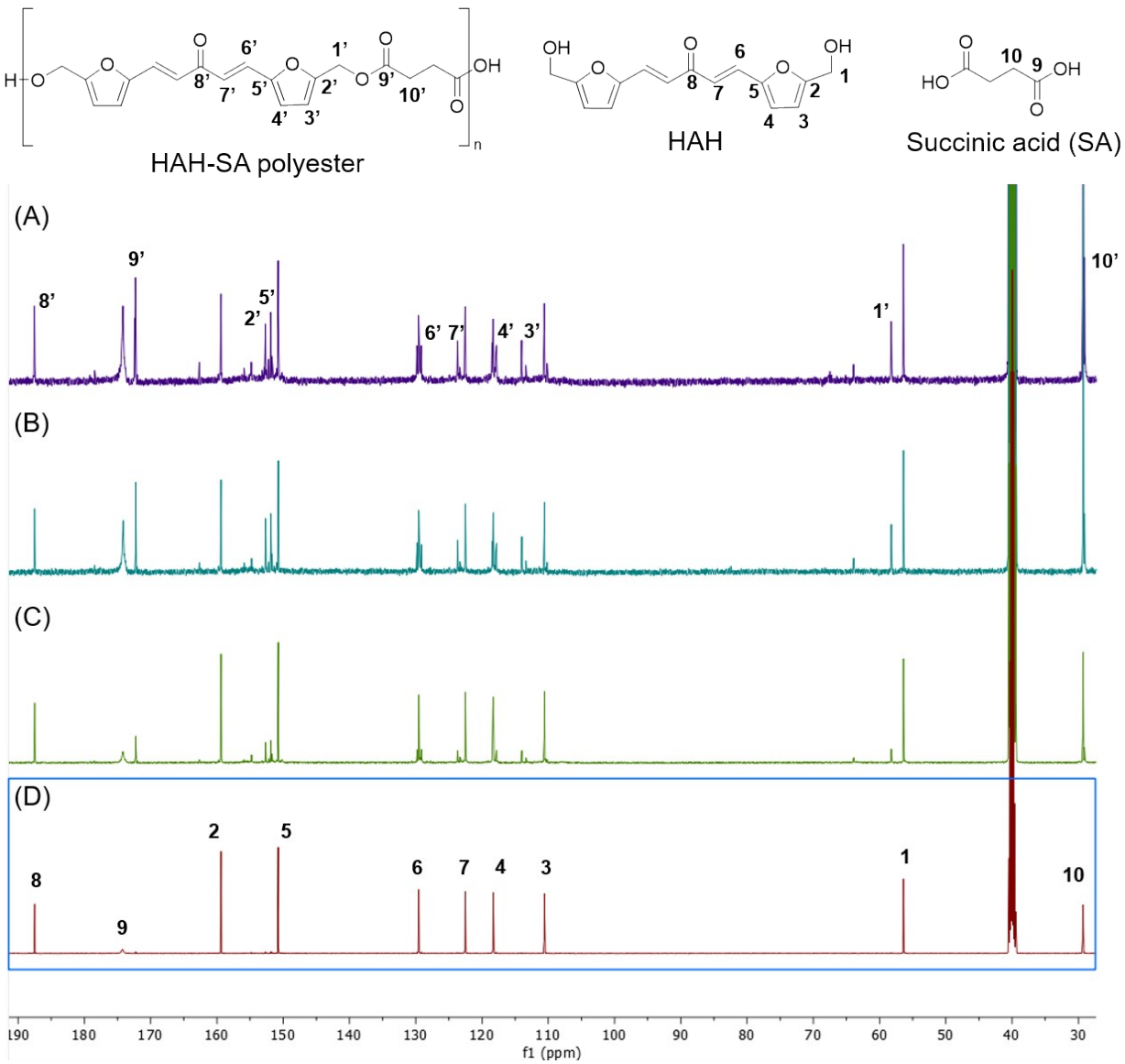

Figure S11. ^{13}C qNMR comparison during HAH-SA polyester synthesis (A) 870 min, (B) 470 min, (C) 300 min, and (D) 60 min after the esterification (Reaction temperature: 130℃).

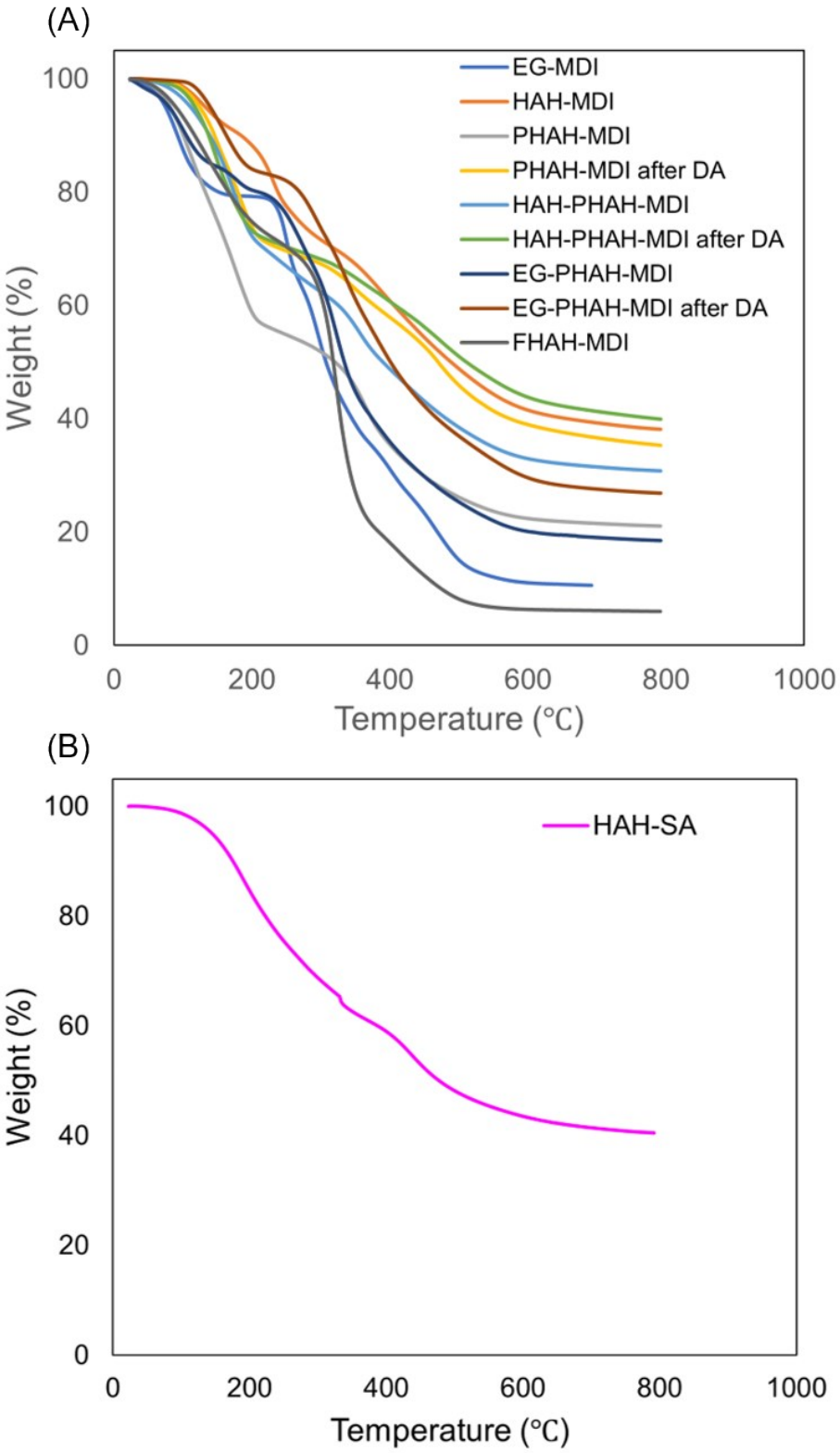

Figure S12. TGA results of (A) polyurethanes (DA abbreviates Diels-Alder reaction) and (B) polyester.

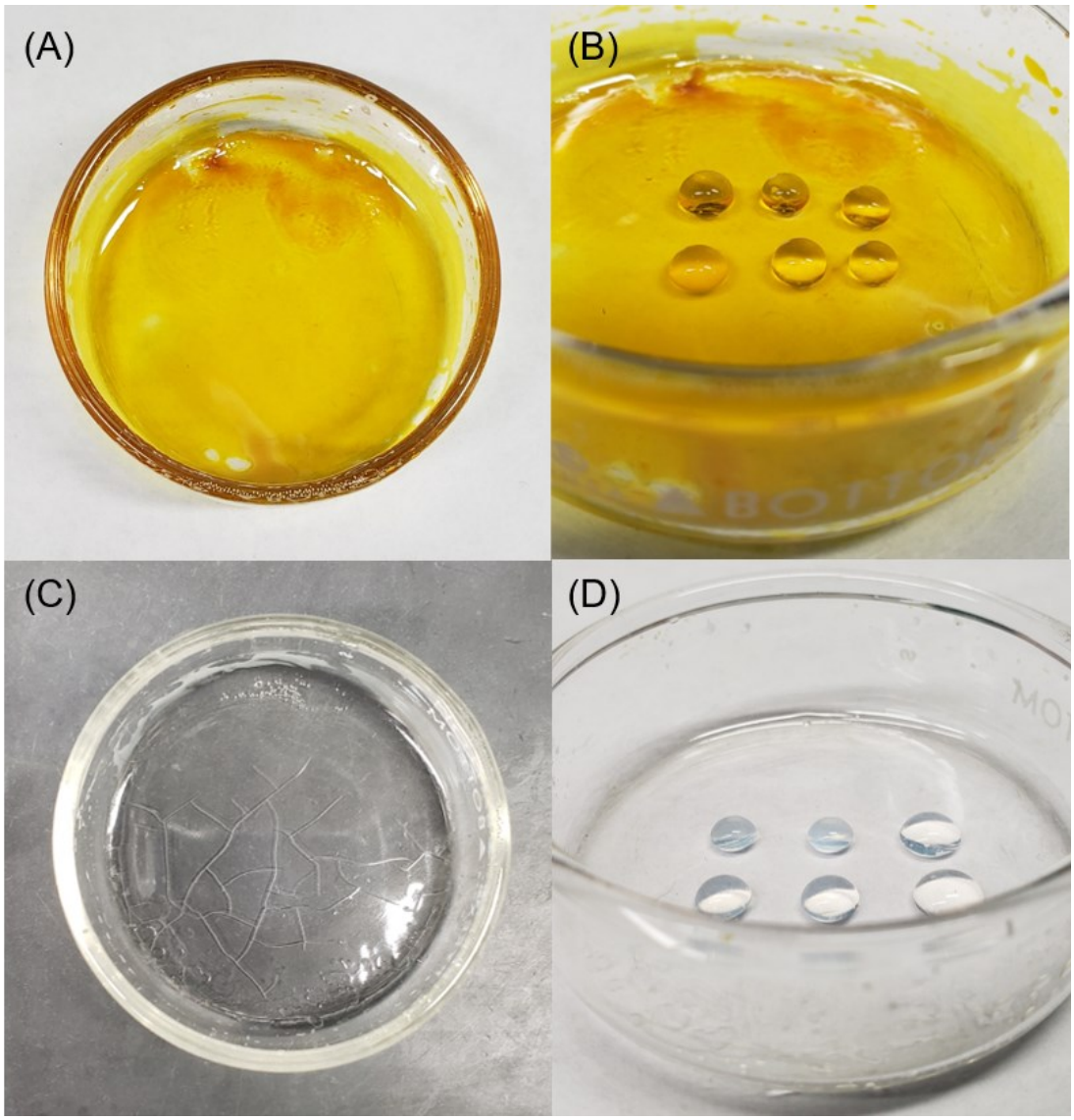

Figure S13. Images of polyurethane-coated glass dishes (A) HAH-MDI coating, (B) HAH-MDI coating with water droplets, (C) FHAH-MDI coating, and (D) FHAH-MDI coating with water droplets.

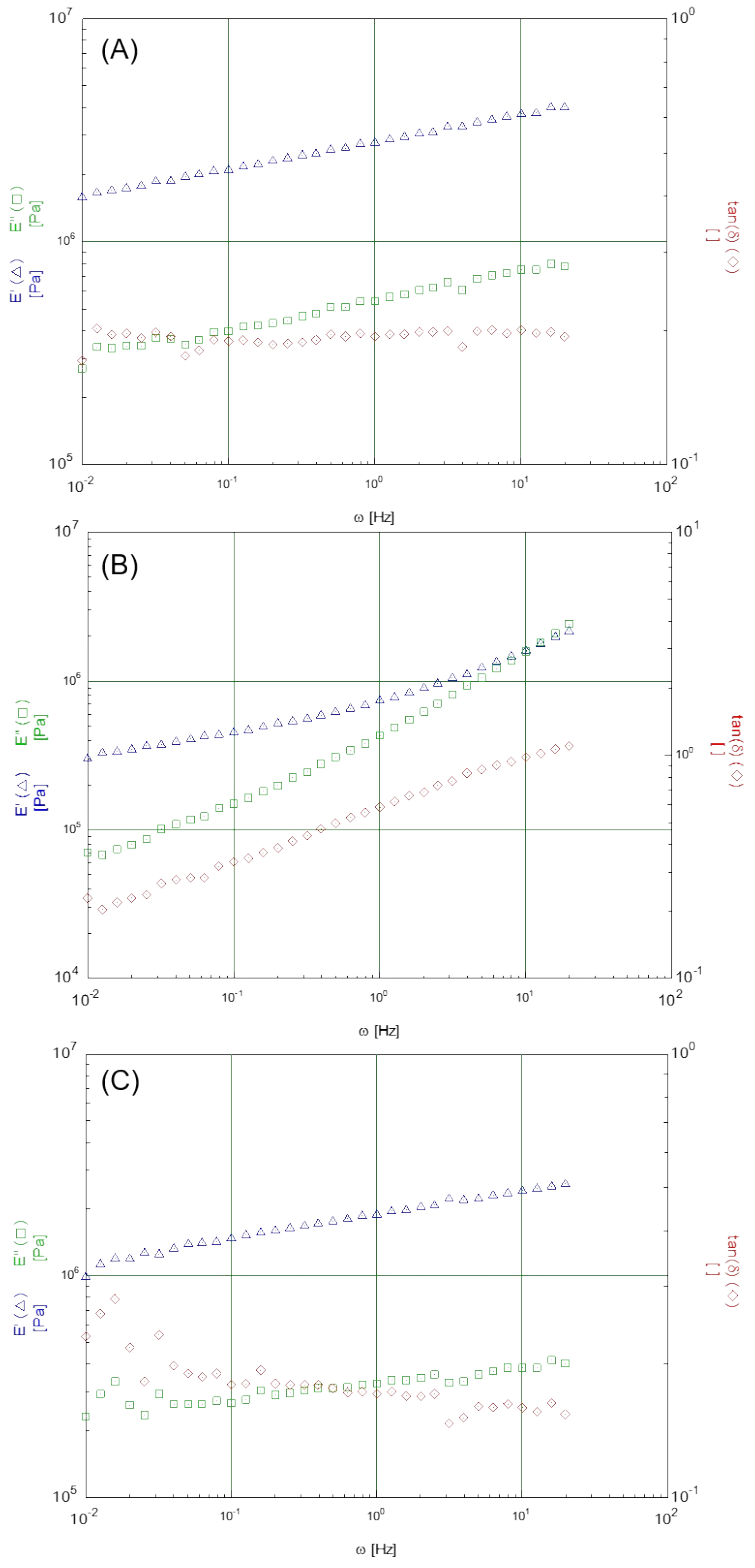

Figure S14. Dynamic frequency sweep test of (A) the molded HAH-MDI polyurethane, (B) the molded FHAH-MDI polyurethane, and (C) the molded HAH-SA polyester (E': Storage modulus, E": Loss modulus, tanδ = E"/E').

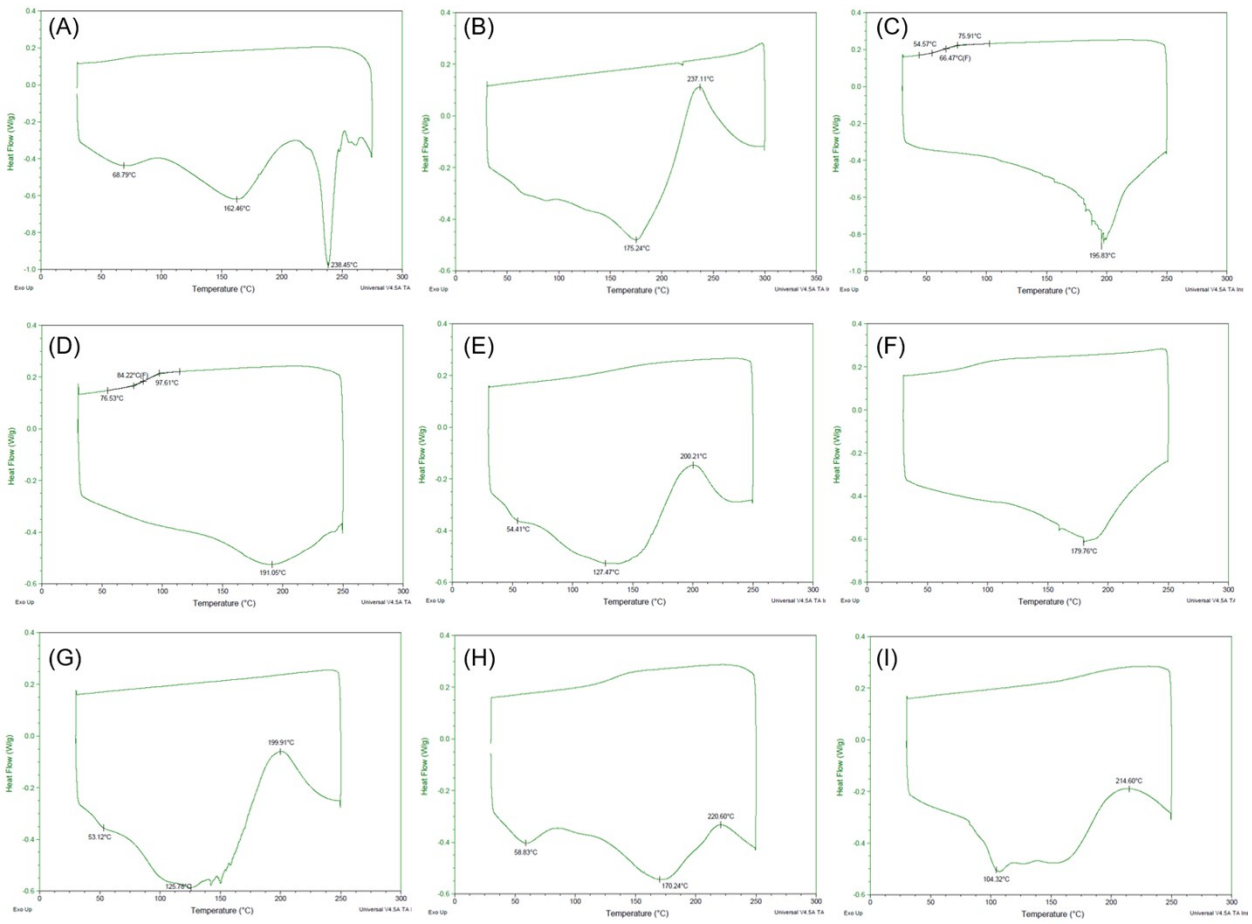

Figure S15. 1st cycle of DSC results of (A) EG-MDI, (B) HAH-MDI, (C) PHAH-MDI, (D) FHAH-MDI, (E) PHAH-MDI after Diels-Alder, (F) HAH-PHAH-MDI, (G) HAH-PHAH-MDI after Diels-Alder reaction, (H) EG-PHAH-MDI, and (I) EG-PHAH-MDI after Diels-Alder reaction (Exothermic process increases heat flow and endothermic process decreases heat flow).

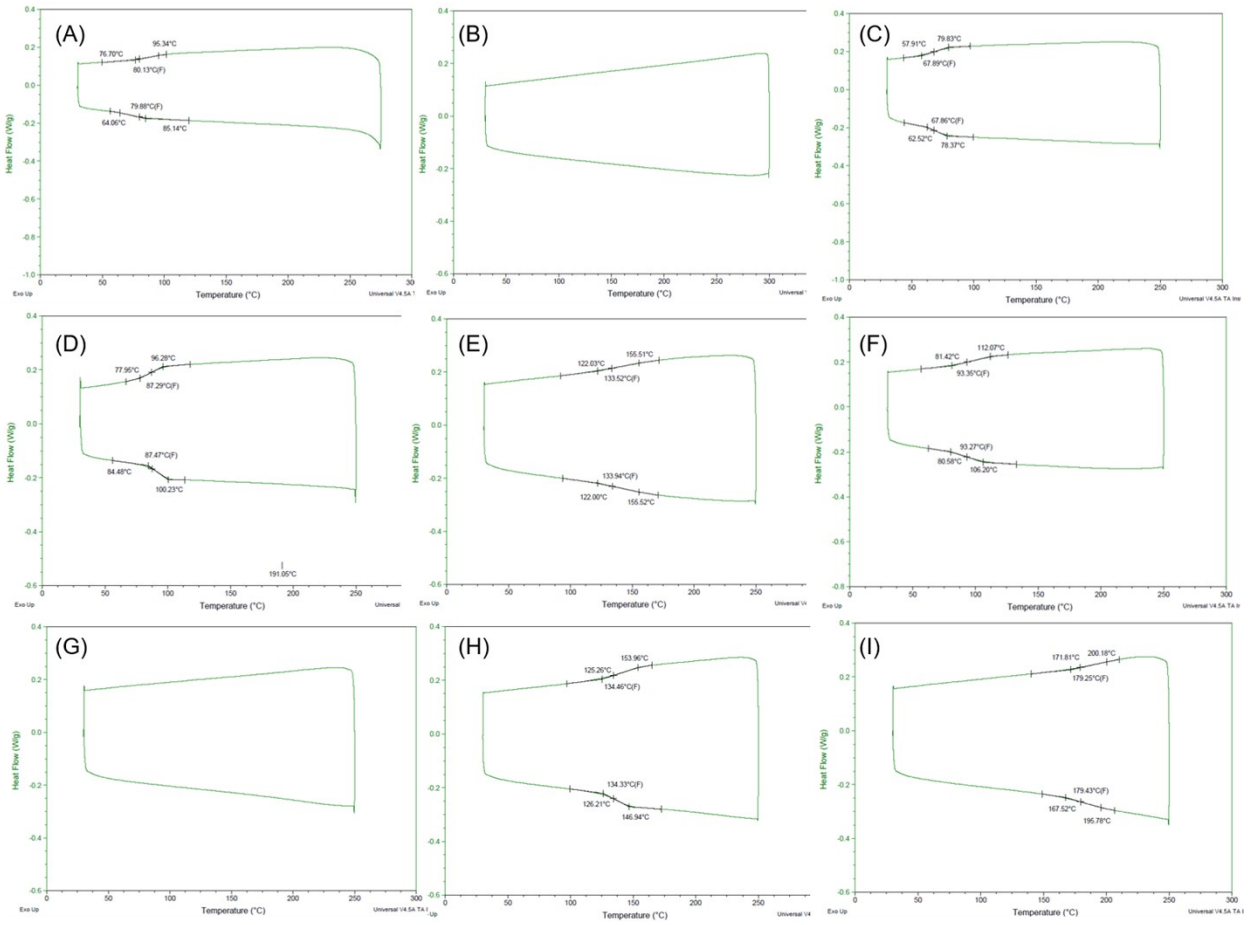

Figure S16. 2nd cycle of DSC results of (A) EG-MDI, (B) HAH-MDI, (C) PHAH-MDI, (D) FHAH-MDI, (E) PHAH-MDI after Diels-Alder reaction, (F) HAH-PHAH-MDI, (G) HAH-PHAH-MDI after Diels-Alder reaction, (H) EG-PHAH-MDI, and (I) EG-PHAH-MDI after Diels-Alder reaction (Exothermic process increases heat flow and endothermic process decreases heat flow).

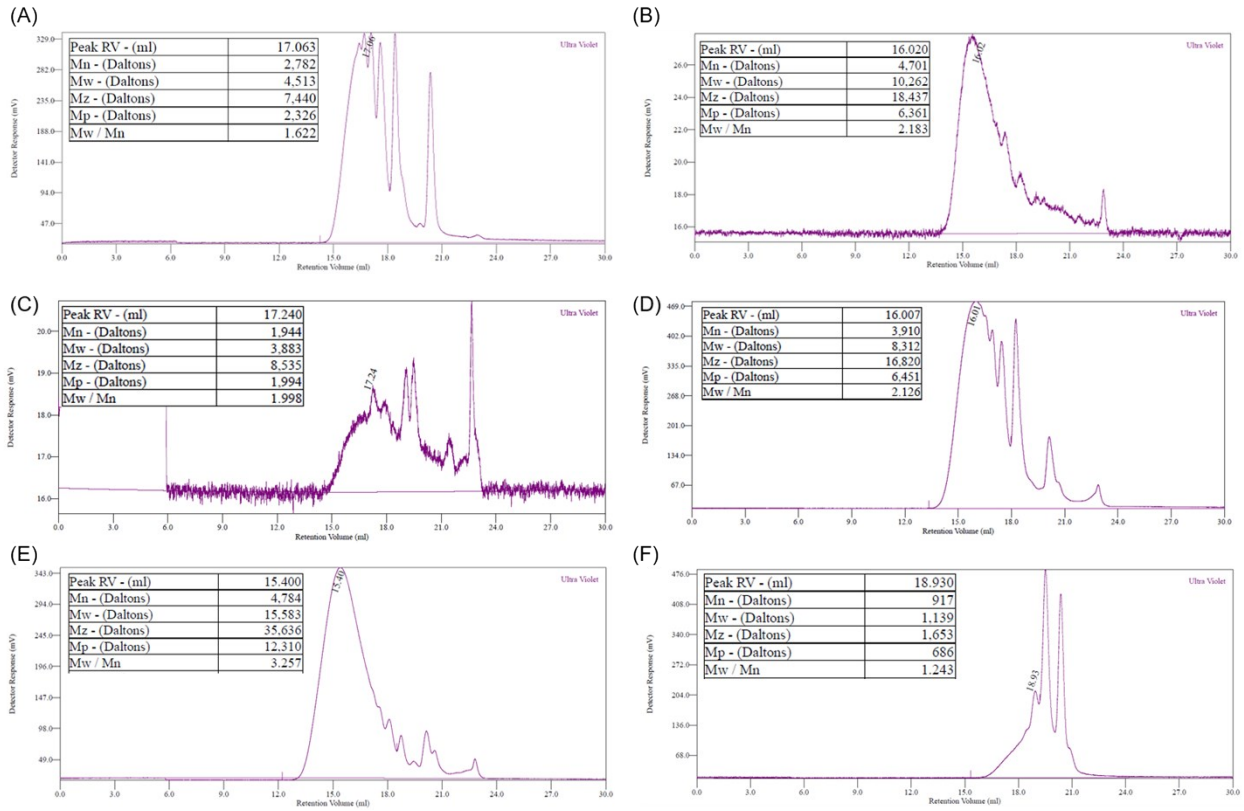

Figure S17. GPC results of THF-soluble oligomers (A) HAH-MDI, (B) PHAH-MDI, (C) FHAH-MDI, (D) HAH-PHAH-MDI, (E) EG-PHAH-MDI, and (F) HAH-SA (UV detector at 390 nm wavelength was used to measure $\bar{MW}$ of HAH-containing oligomers and UV detector at 320 nm wavelength was used to measure $\bar{MW}$ of PHAH or FHAH-containing oligomers; Degree of polymerization = Mn/molecular weight of repeating unit).

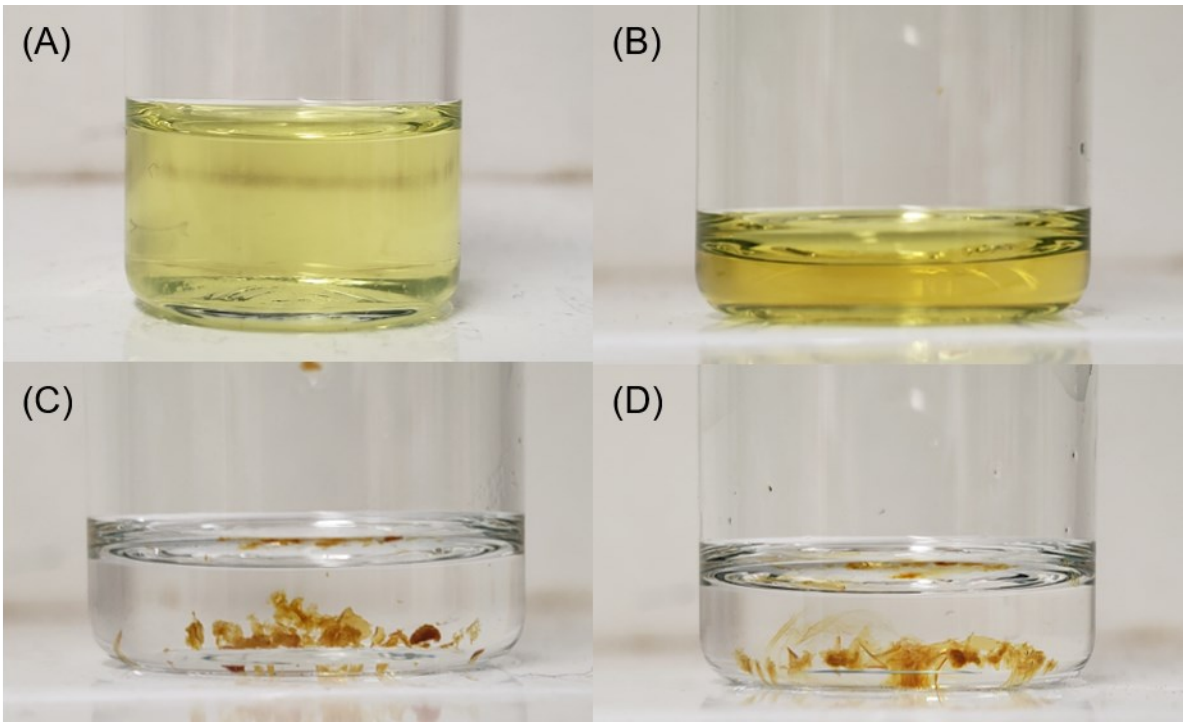

Figure S18. Solubility analyses of homogenous solutions by dissolving 100 mg of bismaleimide in (A) 2.5 mL of THF and (B) 0.5 mL of DMSO at 25℃; Solubility analysis of insoluble polymer by adding 3 mg of EG-PHAH-MDI after Diels-Alder crosslinking sample in (C) 1 mL of THF and (D) 1 mL of DMSO at 25℃.

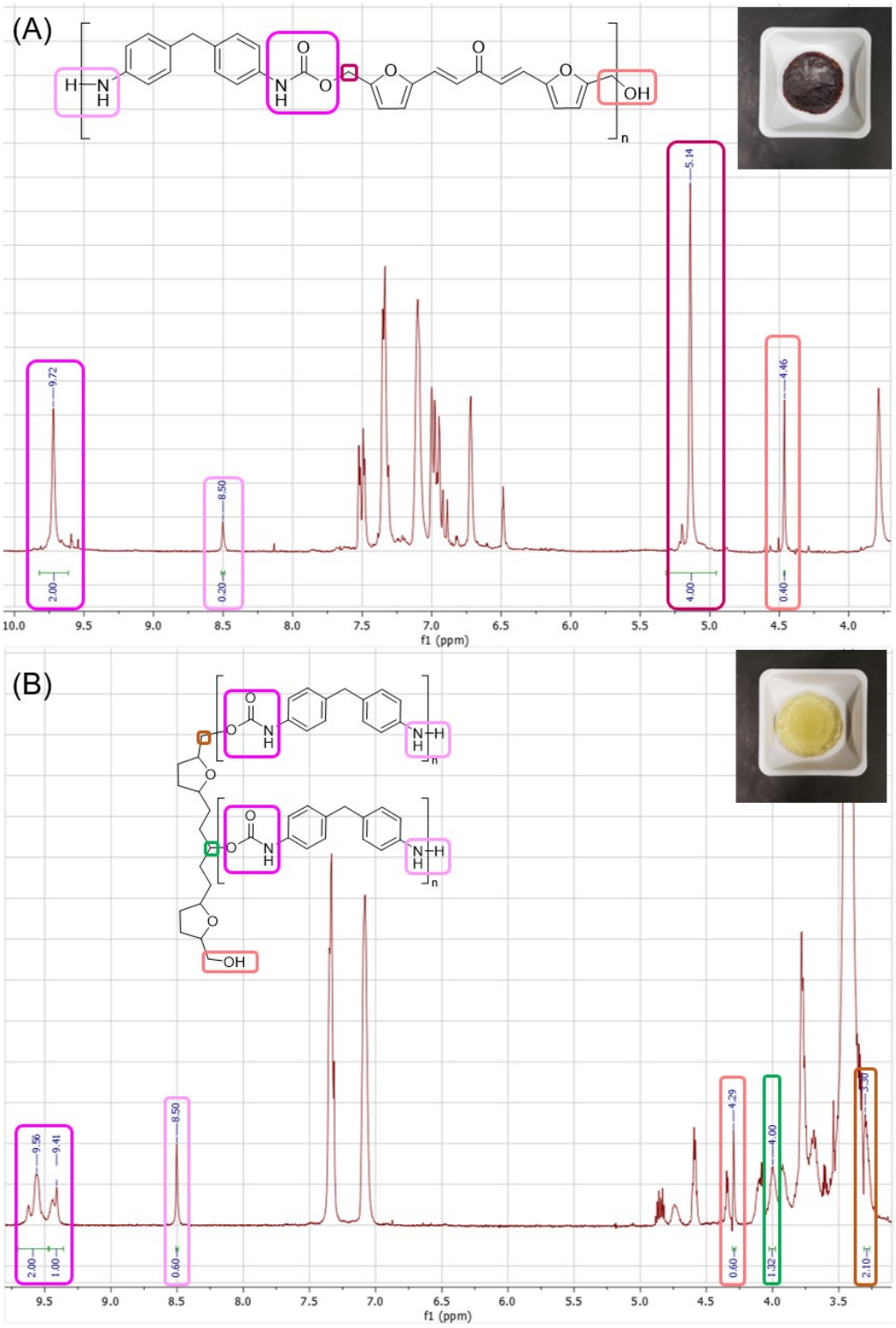

Figure S19. Degree of polymerization (DP) analysis of (A) molded HAH-MDI (CH_2OH group : NHCOO group (mol) = 0.40/2 (4.46 ppm) : 2.00 (9.72 ppm); DP=10), and (B) molded FHAH-MDI (CH_2OH group : NHCOO group (mol) = 0.60/2 (4.29 ppm) : 3.00 (9.56-9.41 ppm); DP=10) by ^1H NMR spectrum (Degree of polymerization was defined by ratio of NHCOO group to CH_2OH group).

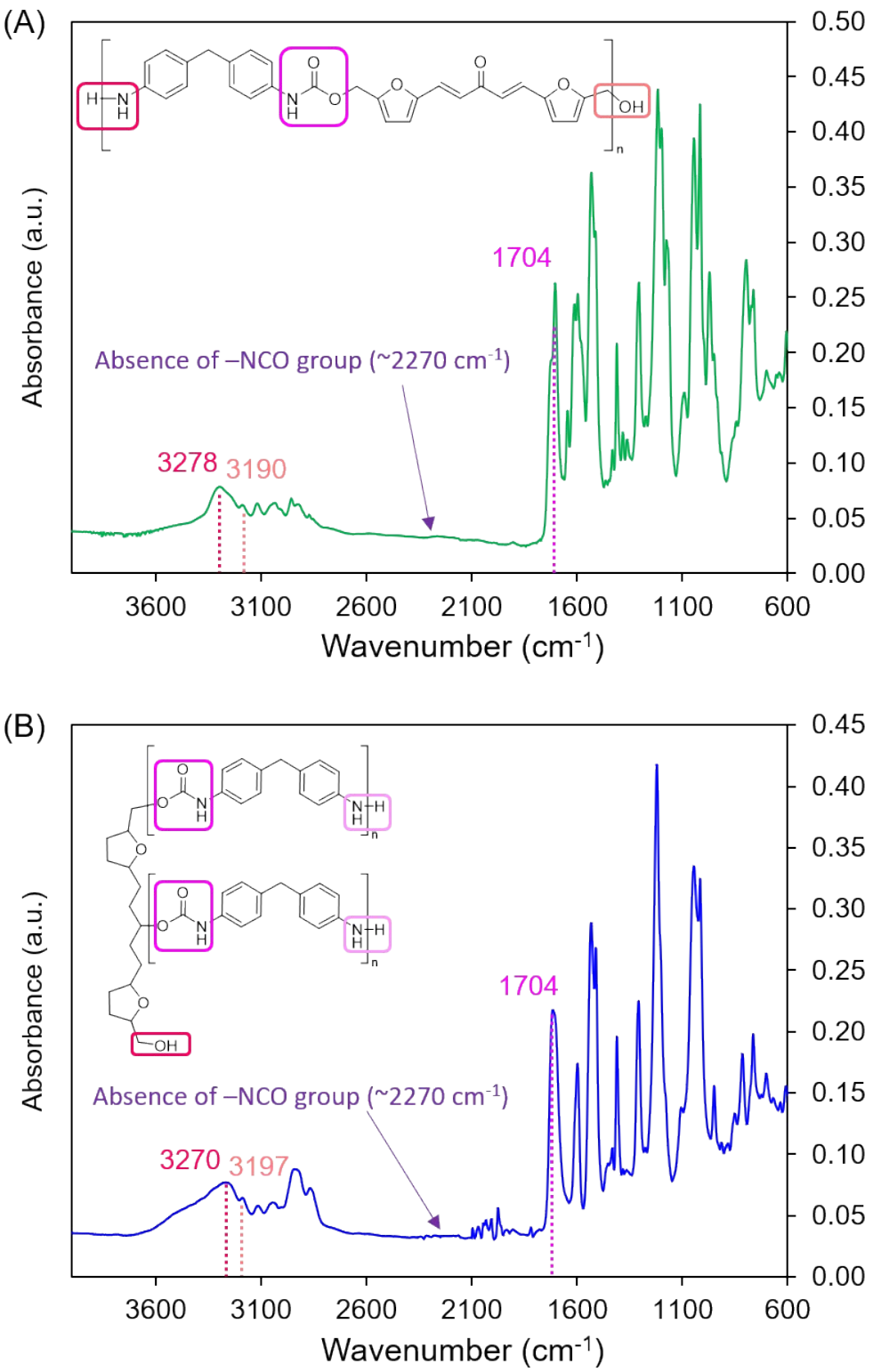

Figure S20. ATR-FTIR analysis of the (A) molded HAH-MDI and (B) molded FHAH-MDI.