Supplementary Information

Design of closed-loop recycling production of a Diels-Alder polymer from a biomass-derived difuran as a functional additive for polyurethanes

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Experimental methods

Analytical methods

HPLC analysis of hydrolyzed solutions. The chemical concentrations of hydrolyzed solutions were quantified by high performance liquid chromatography (HPLC) analysis. The hydrolyzed solution was centrifuged (2500 rpm, 5min) to separate the precipitates from aqueous phase solution. 0.050 g of the aqueous solution was diluted in 0.449 g of Milli-Q water (10 times dilution by volume) to analyze the concentrations of the monomers produced (HMF, pentaerythritol, levulinic acid, maleic acid) from the Diels-Alder polymer. The solid precipitates were dissolved in 2 mL of THF and 0.044 g of solution was further diluted in 0.395 g of THF to analyze the concentration of bismaleimide. All diluted samples were filtered through a 0.2 μm PTFE filter before the sample was injected into the HPLC. The concentrations of pentaerythritol and levulinic acid were measured by a Water 2695 separation module equipped with an Aminex HPX-87H (Bio-Rad) column and RI detector, while the HMF and maleic acid concentrations were measured with a Waters 2998 PDA detector, set at 320 and 230 nm, respectively. The temperature of the HPLC column was maintained at 50℃, and the flow rate of the mobile phase (pH 2 water, acidified by sulfuric acid) was 0.6 mL. The concentration of bismaleimide was measured by a Water 2695 separation module equipped with a Luna C18 (Phenomenex) column and a Water 2998 PDA detector, set at 320 nm. The temperature of the HPLC column was held constant at 50℃. The mobile phase was a gradient of methanol/water (with 0.1 wt% formic acid) at a constant flow rate of 1.0 mL min^{-1} (0.1 wt% formic acid water linearly changed to methanol in 20 min, held pure methanol for 7 min, and methanol linearly changed to 0.1 wt% formic acid water in 3 min).

GPC analysis of Diels-Alder oligomers. Gel permeation chromatography (GPC) analysis was performed by using a Viscotek GPCmax/VE 2001 instrument fitted with PolyPore columns (2×300×7.5 mm) featuring 5 μm particle size from Polymer Laboratories. Liquid solution, containing the Diels-Alder oligomers in THF, was eluted with THF at a flow rate of 1 mL·min^{-1} at 40℃. The molecular weights of the oligomers were characterized by UV (at 390 nm wavelength) detection using a Viscotek Model 302-050 Tetra Detector Array. Omnisec software (Viscotek, Inc.) was used for data processing such as positioning the baseline, setting limits, and applying the molecular weight calibration.

NMR analysis of the monomers and Diels-Alder polymer. ^{1}H Nuclear magnetic resonance (NMR), ^{13}C NMR, and HSQC NMR spectra were obtained using a Brucker Avance-500 spectrometer. Tetramethylsilane (TMS) (δ: 0 ppm) was used as a reference for chemical shifts.

DSC analysis of Diels-Alder polymer. Differential scanning calorimetry (DSC) measurements (TA Instruments Q100 modulated differential scanning calorimeter, New Castle, DE) was used to investigate the phase transition of polyurethanes with a heating and cooling rate of 10℃ min^{-1}. 5 mg of Diels-Alder polymer, Diels-Alder polymer-MDI, Diels-Alder polymer-EG-MDI, and EG-MDI were placed in a standard aluminum pan (TA instrument) and sealed with a standard aluminum lid (TA instrument) to prepare DSC samples. Empty standard aluminum pan and lid were sealed and used as a reference. The heating and cooling cycles were repeated 3 times between 30 to 200℃ (30 to 270℃ for EG-MDI) under 50 mL min^{-1} of N$_2$ gas flow. 2 min at constant temperature was allowed at the end of the heating and cooling process. DSC data were analyzed by TA Universal Analysis software. Glass transition temperatures and specific heat capacities of polymers were measured by the 2nd heating and cooling processes of the DSC. The specific heat capacity was calculated from the DSC result by using the equation: Specific heat capacity (C$_p$, J ℃$^{-1}$g^{-1}) = Heat flow (W g^{-1}) * 60 (s min^{-1}) / Heating rate (10℃ min^{-1}).

TGA analysis of Diels-Alder polymer. TA Instruments Q500 Thermogravimetric Analyzer (TGA) was used to measure the thermal stabilities of polyurethanes. 10 mg of Diels-Alder polymer were put in a 10 mm platinum sample pan with stirrup (Instrument Specialists Inc.) and placed in the furnace. The ramp rate was set to 20℃ min^{-1} from 25℃ to 700℃ under 50 mL min^{-1} of N$_2$ gas flow. TGA data were analyzed by TA Universal Analysis software.

ATR-FTIR analysis of molded polyurethanes. Attenuated total reflectance FTIR measurements (ATR-FTIR) were taken on a Bruker Vertex 70 equipped with a liquid nitrogen-cooled MCT detector. The ATR cell used was a MIRacle single reflection cell equipped with a diamond crystal (Pike Technologies). 20 mg of the Diels-Alder polymer, HPH monomer, and bismaleimide were placed in the ATR cell for the measurement. In a typical measurement, 128 scans were averaged with a 4 cm^{-1} resolution.
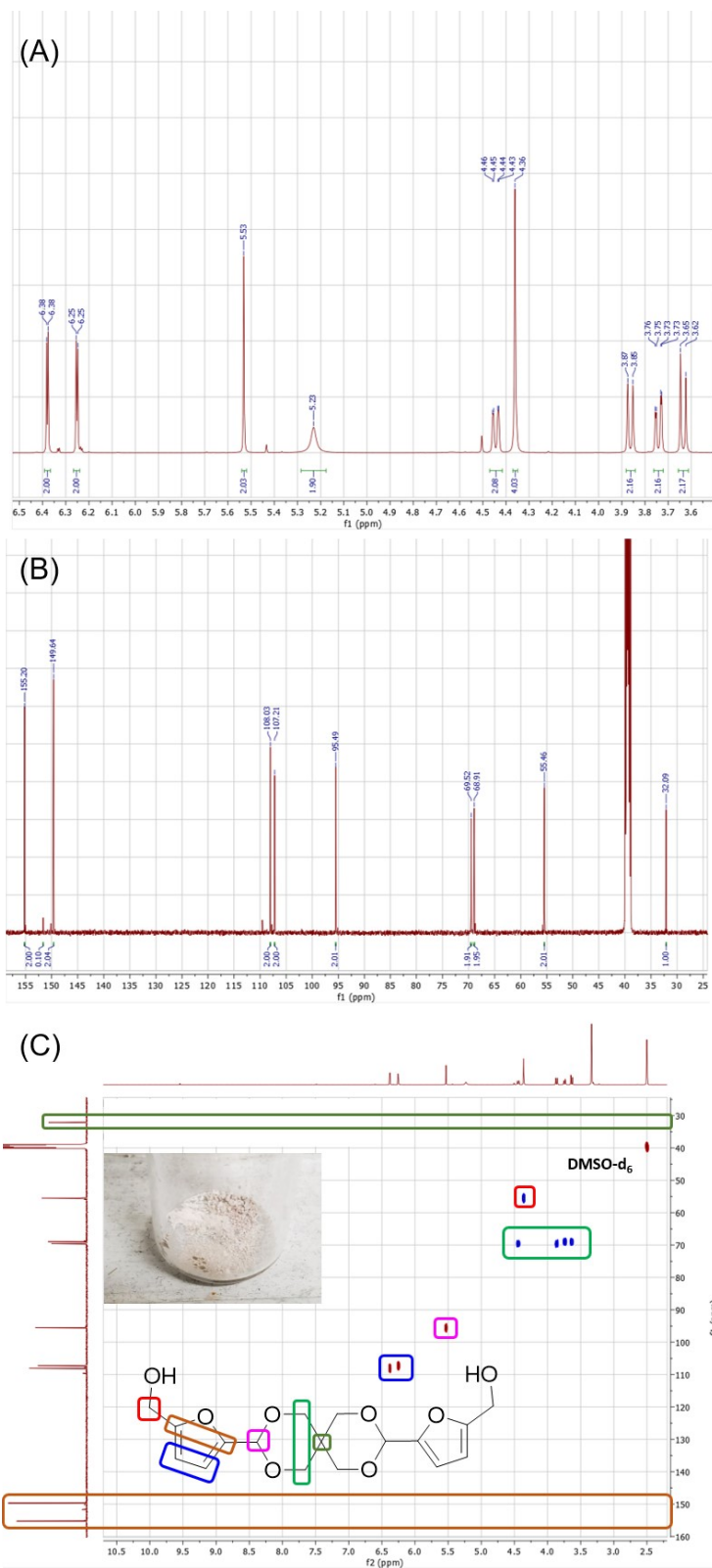
Fig.S1. (A) ^{1}H NMR spectrum, (B)^{13}C qNMR spectrum, and (C) HSQC spectrum of HPH monomer and its molecular structure (Inset image shows the purified HPH).
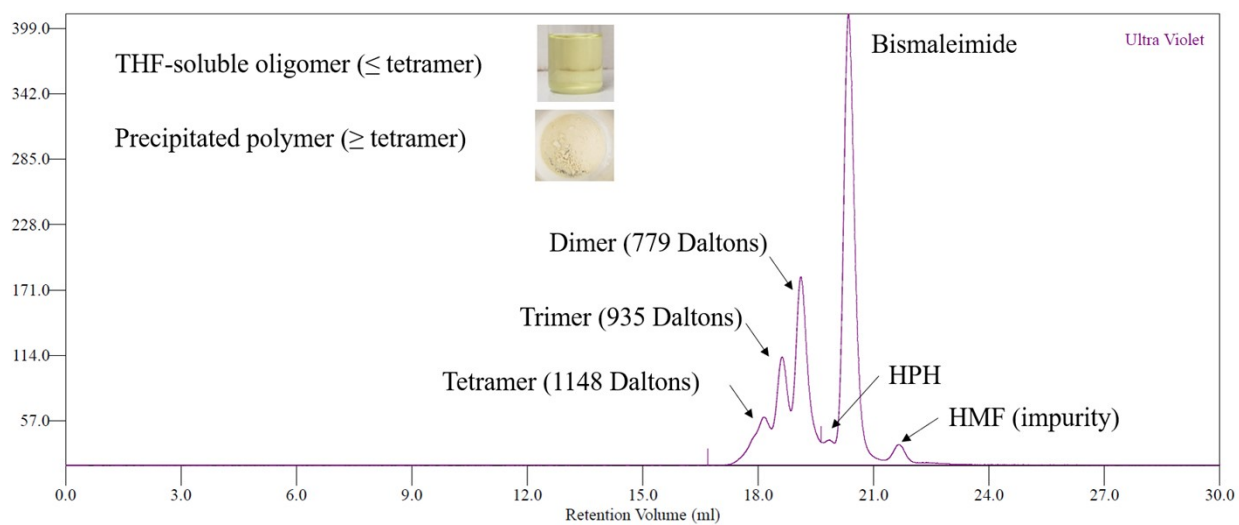
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Fig.S2. GPC analysis of THF-soluble Diels-Alder adducts from HPH and bismaleimide; Inset images show the THF-soluble oligomer and the precipitated polymer.
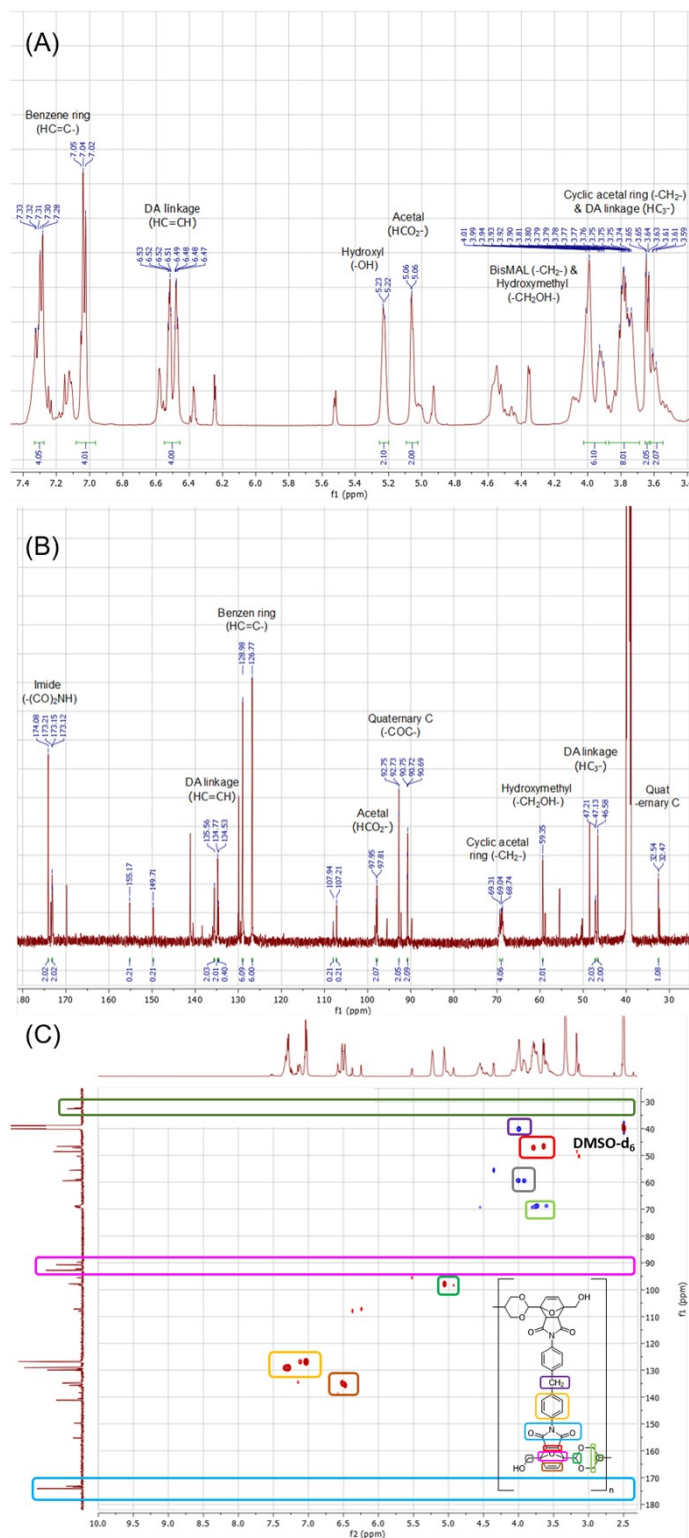
Fig.S3. (A) ^{1}H NMR spectrum, (B)^{13}C qNMR spectrum, and (C) HSQC spectrum of the Diels-Alder polymer (in DMSO-d$_6$) and its structure (By ^{13}C qNMR, Terminal maleimide moiety (134.53 ppm) : Terminal furan moiety (107.94-107.21 ppm) : Diels-Alder adduct bond (47.21-46.58 ppm) = 0.40 : 0.40 : 4.00 (mol), Degree of polymerization = 10).
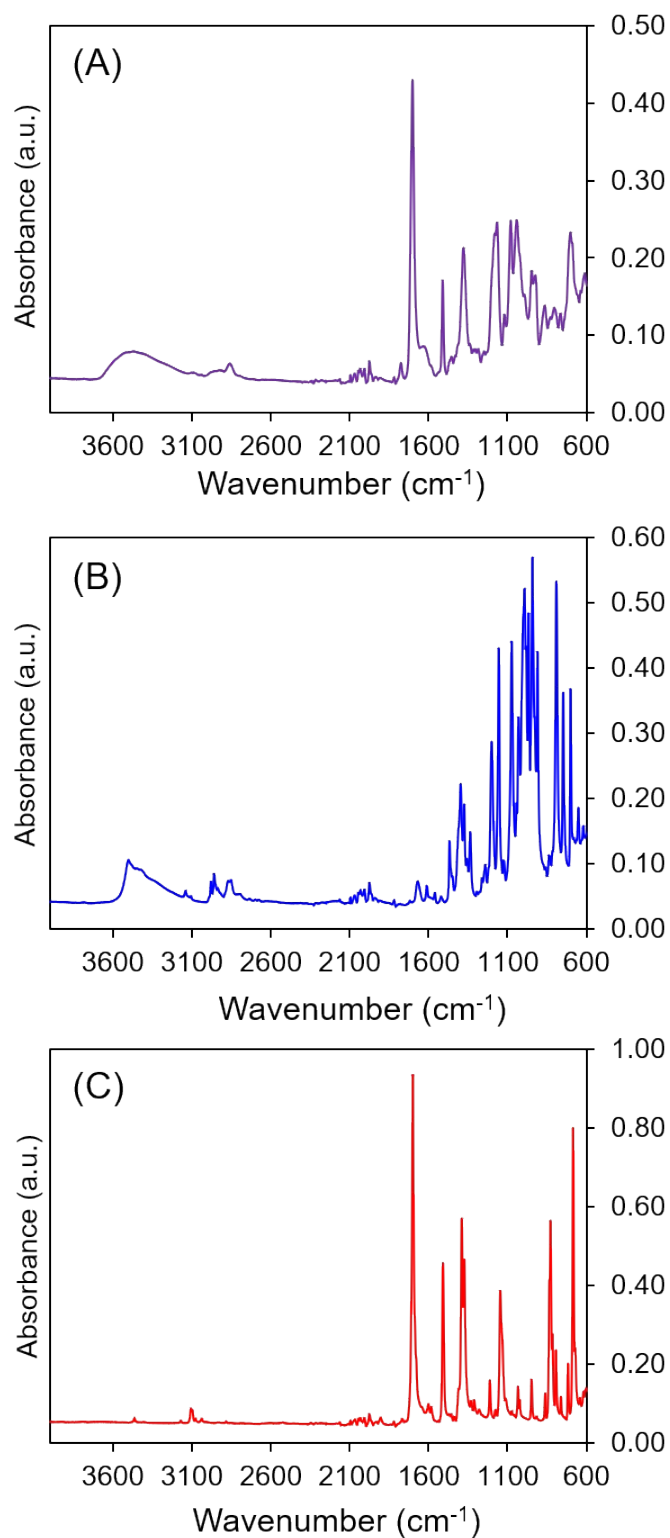
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Fig.S4. ATR-FTIR spectrum of (A) Diels-Alder polymer, (B) HPH monomer, and (C) bismaleimide monomer.
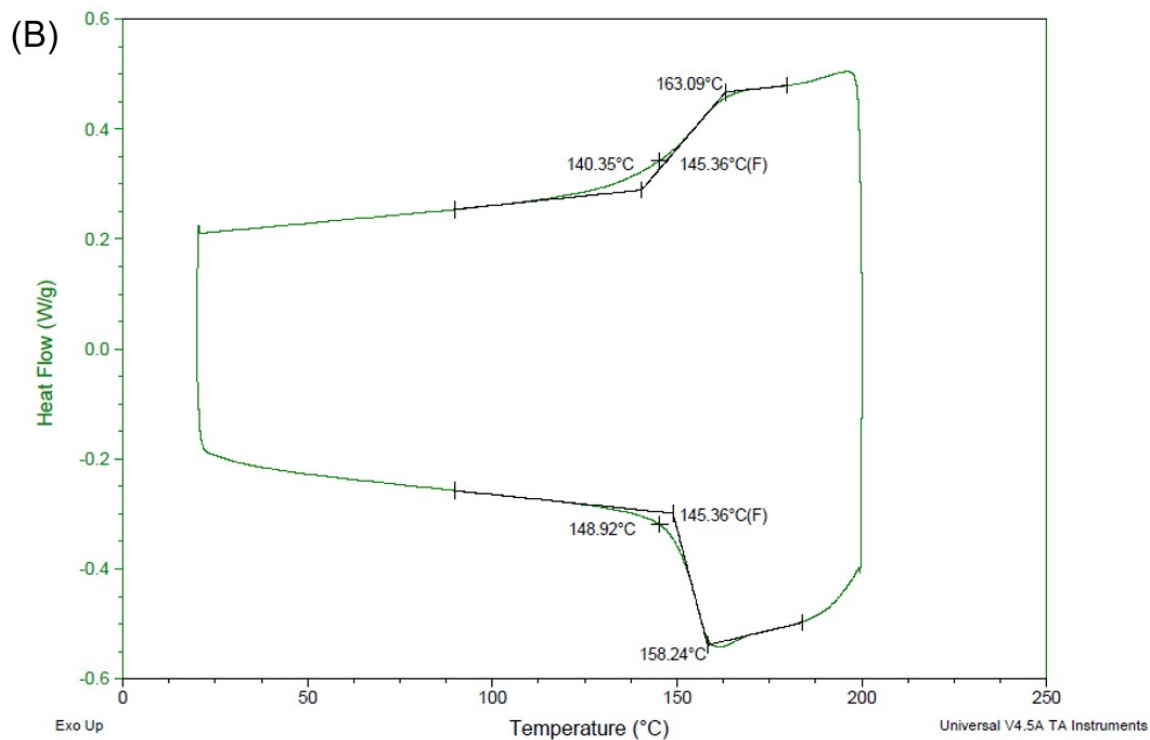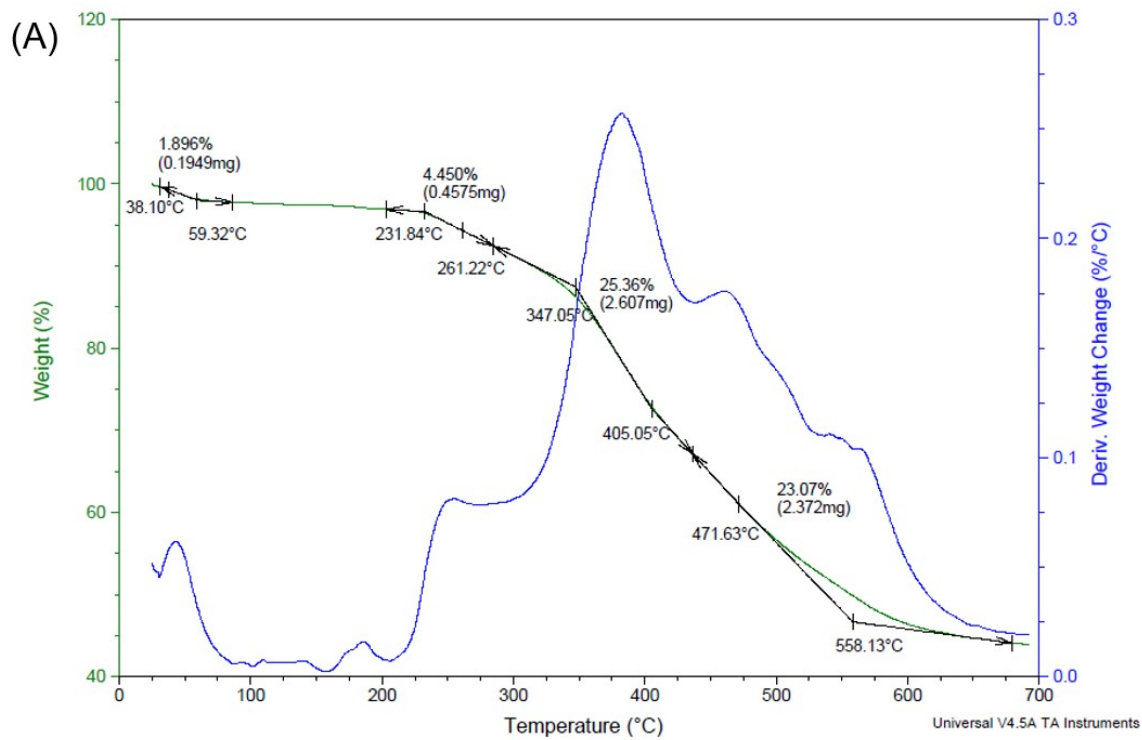
Fig.S5. (A) TGA and (B) DSC (2nd cycle of heating and cooling process) analysis of Diels-Alder polymer.
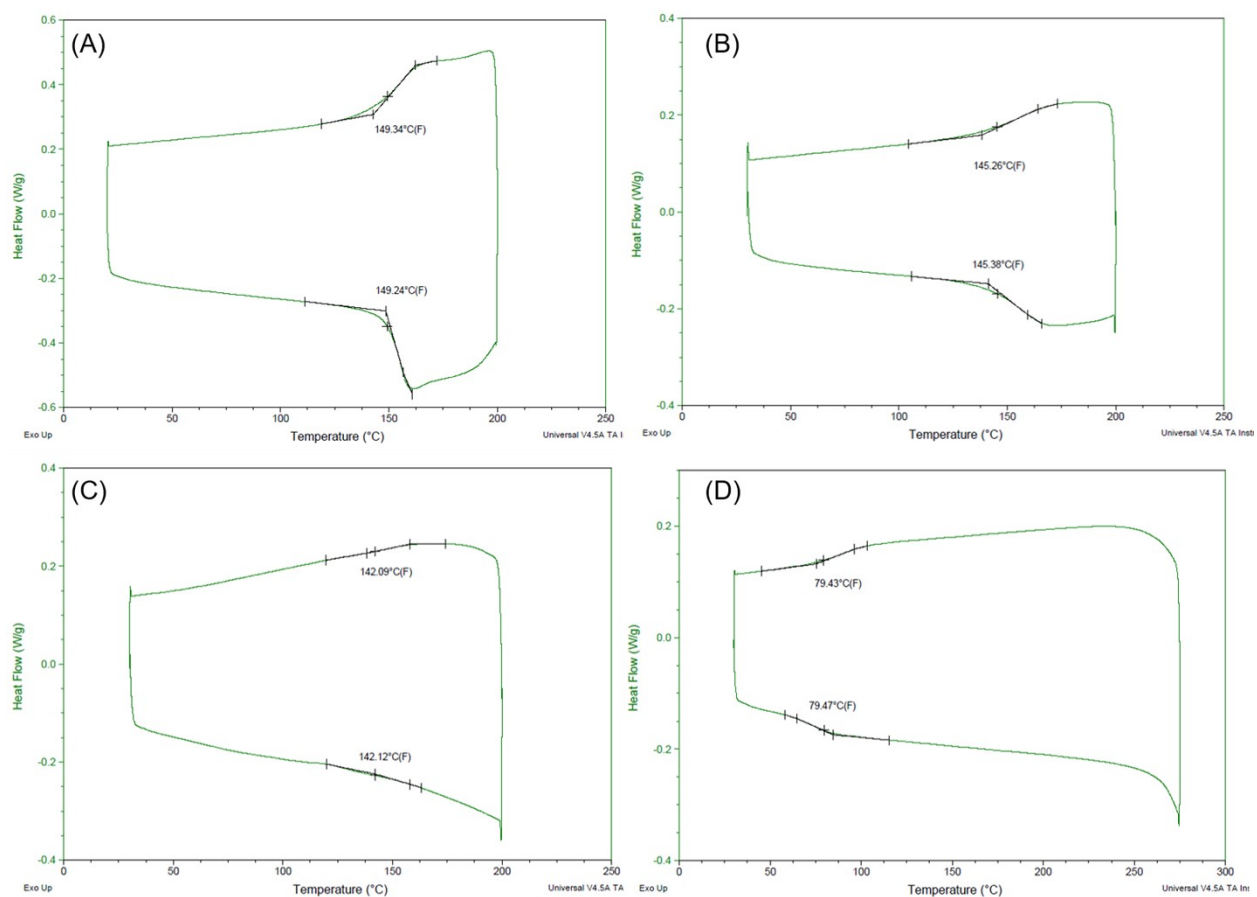
Fig.S6. DSC (2nd heating and cooling cycle) analysis of (A) Diels-Alder polymer, (B) Diels-Alder polymer-MDI, (C) Diels-Alder polymer-EG-MDI, and (D) EG-MDI.
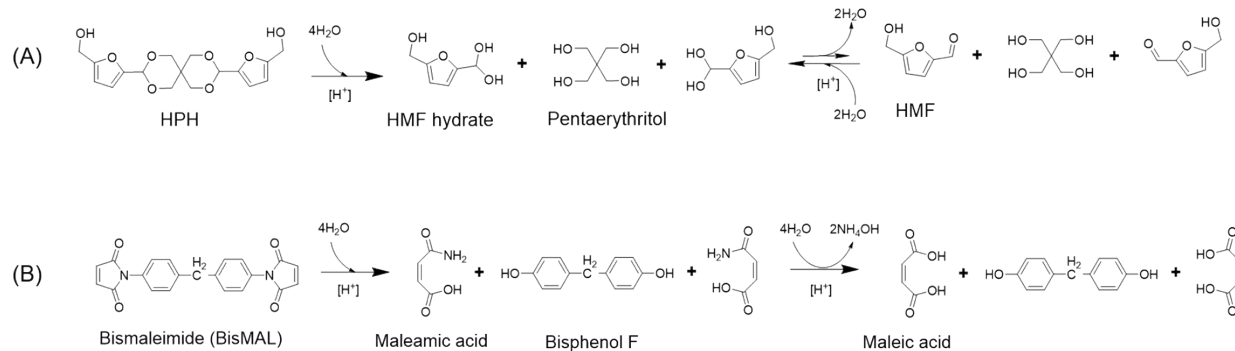

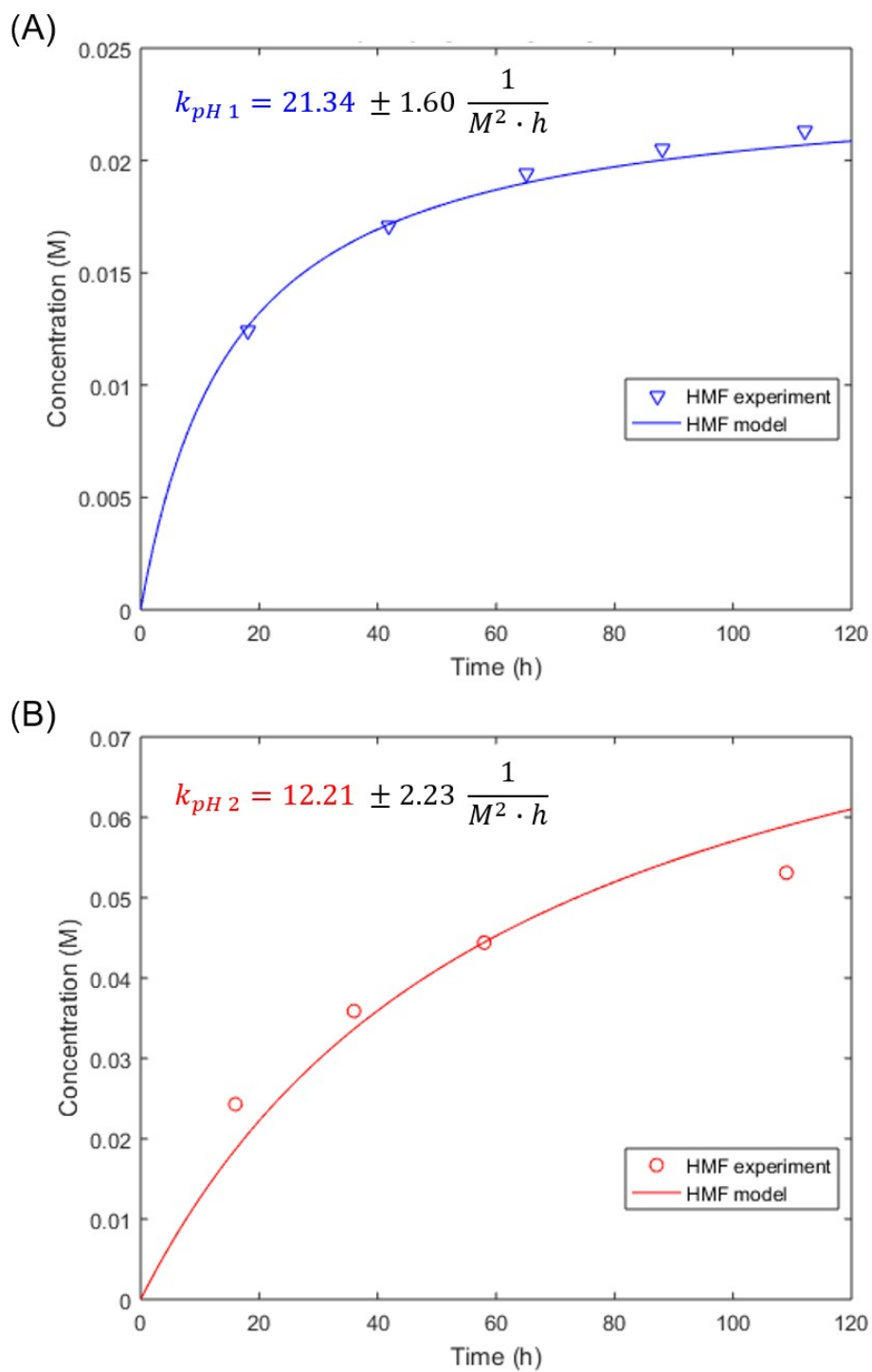**Fig.S7.** Hydrolysis mechanism of (A) HPH and (B) bismaleimide.

(A)

(B)

Fig.S8. Kinetic model for hydrolysis of Diels-Alder polymer under (A) pH1 and (B) pH2 acetate buffer at 60°C.
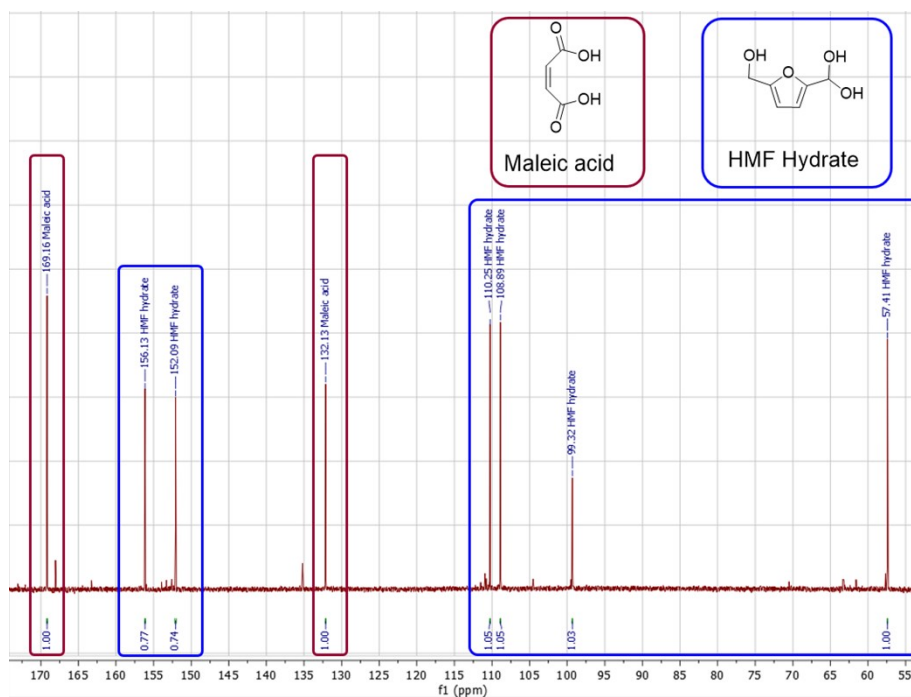
Fig.S9. ^{13}C qNMR (126 MHz, MeOD) of the recovered monomers in EtOAc fraction (Maleic acid: 169.13 (1C), 132.13 (1C) ppm; HMF hydrate: 156.13 (1C), 152.09 (1C), 110.25 (1C), 108.89 (1C), 99.32 (1C), 57.41 (1C) ppm).
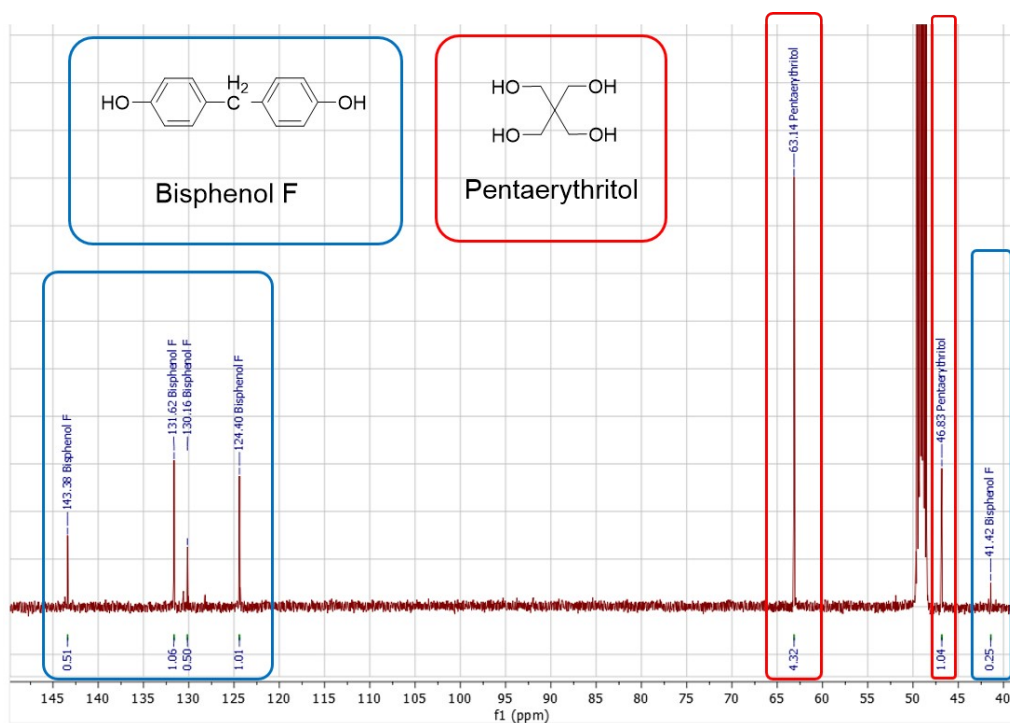
Fig.S10. ^{13}C qNMR (126 MHz, MeOD) of the recovered monomers in aqueous fraction (Bisphenol F: 143.38 (2C), 131.62 (4C), 130.16 (2C), 124.40 (4C), 41.42 (1C) ppm; Pentaerythritol: 63.14 (4C), 46.83 (1C) ppm).

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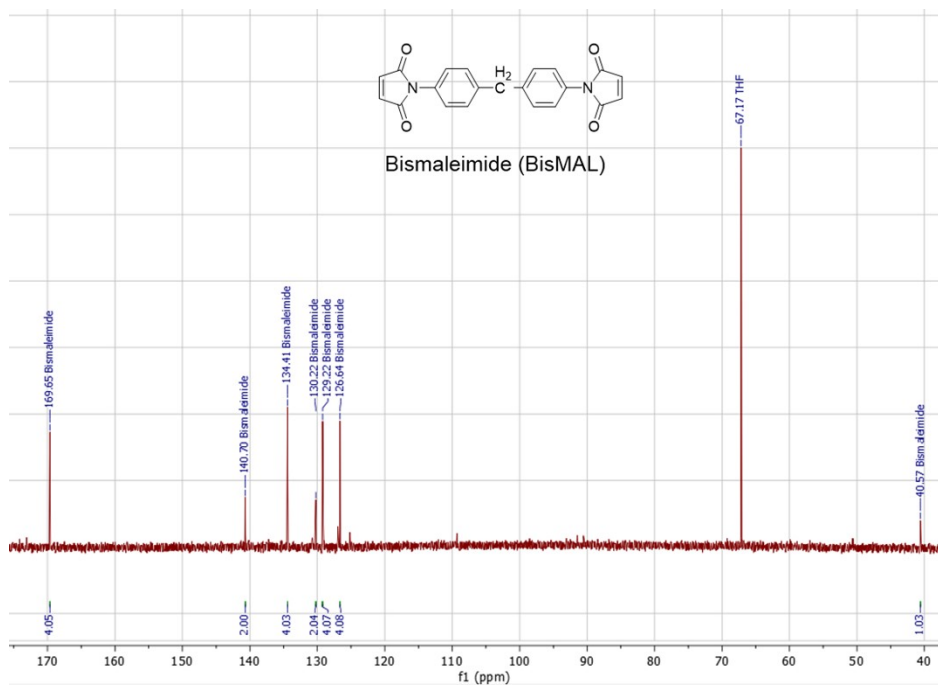
Fig.S11. ^{13}C qNMR (126 MHz, Acetone-d$_6$) of the recovered monomer in acetone fraction (Bismaleimide: 169.65 (4C), 140.70 (2C), 134.41 (4C), 130.22 (2C), 129.22 (4C), 126.64 (4C), 41.42 (1C) ppm).
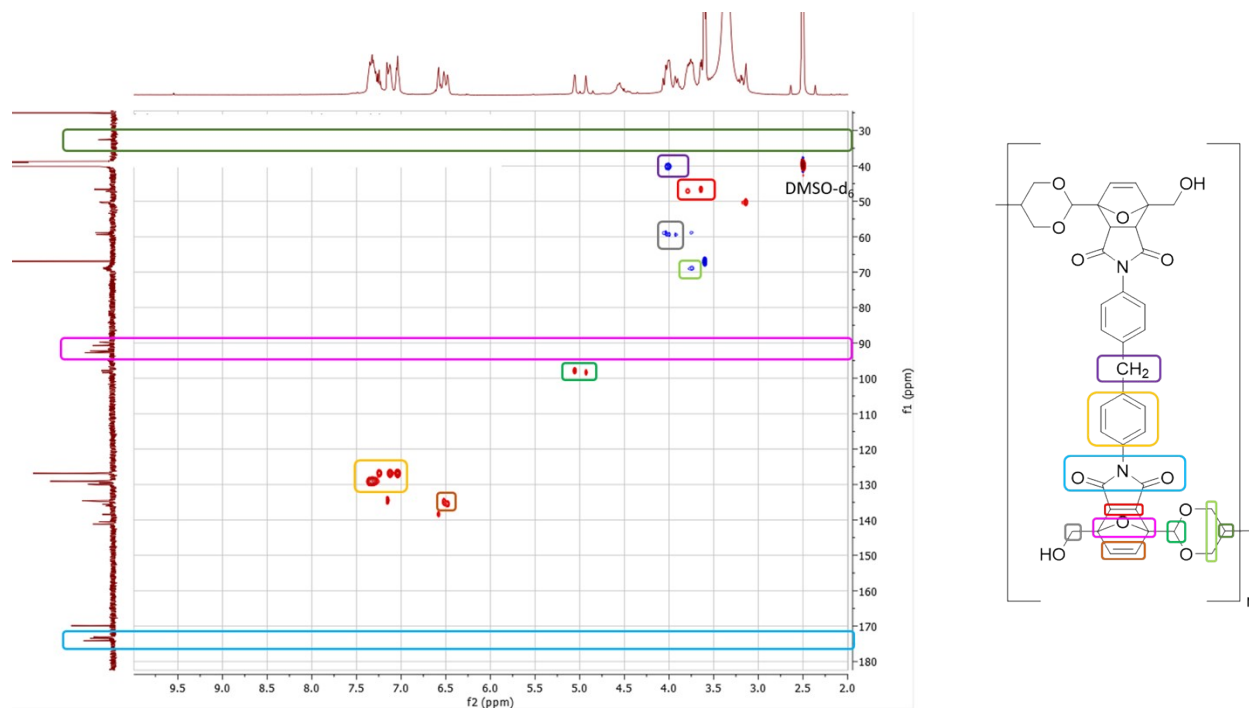
Fig.S12. HSQC spectrum of the recovered Diels-Alder polymer in solid fraction.
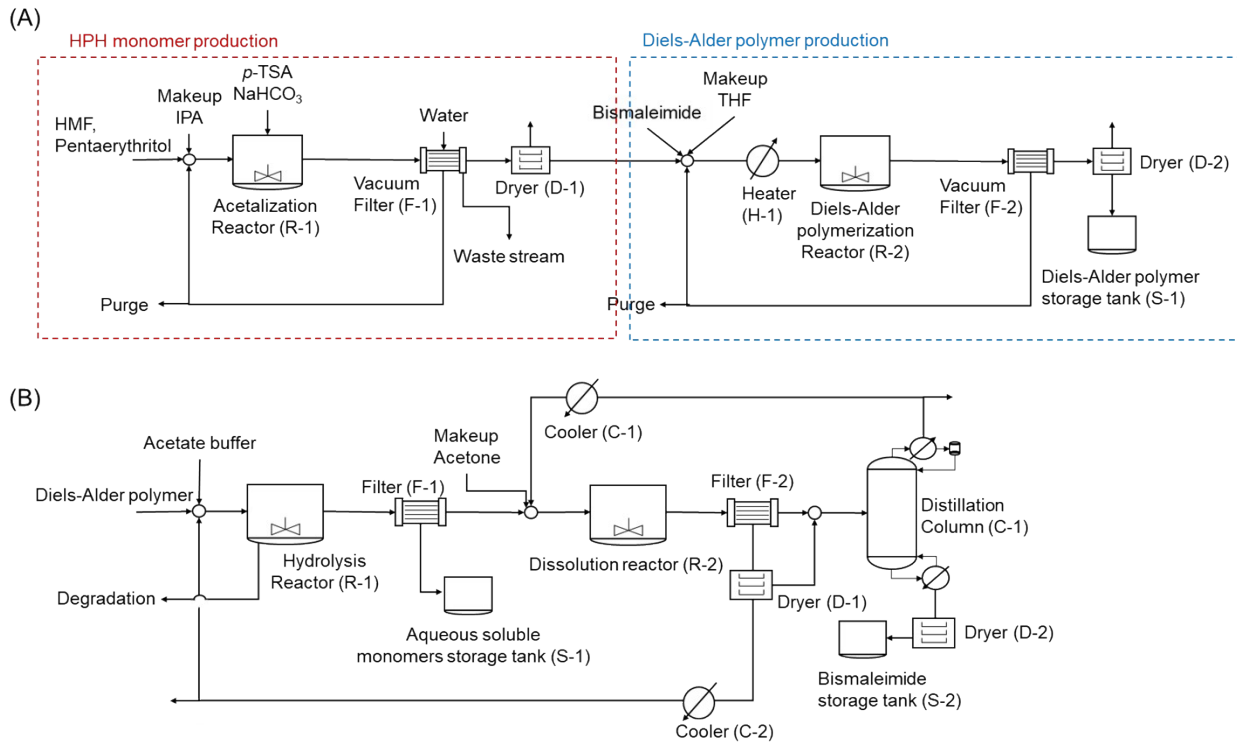
Fig.S13. Process flow diagrams of (A) Diels-Alder polymer production and (B) bismaleimide recovery.
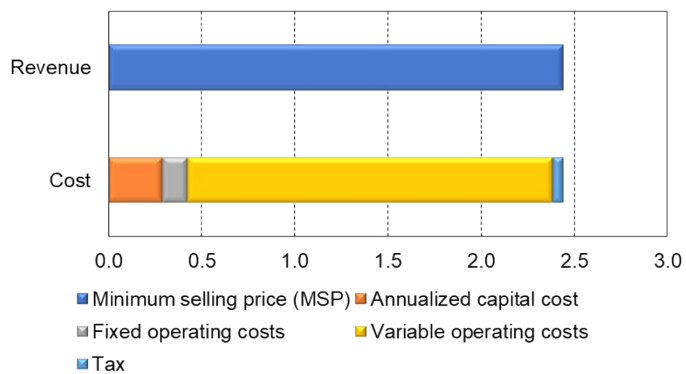
Fig.S14. Cost breakdown of bismaleimide recovery at 28.7 kton of annual bismaleimide production.
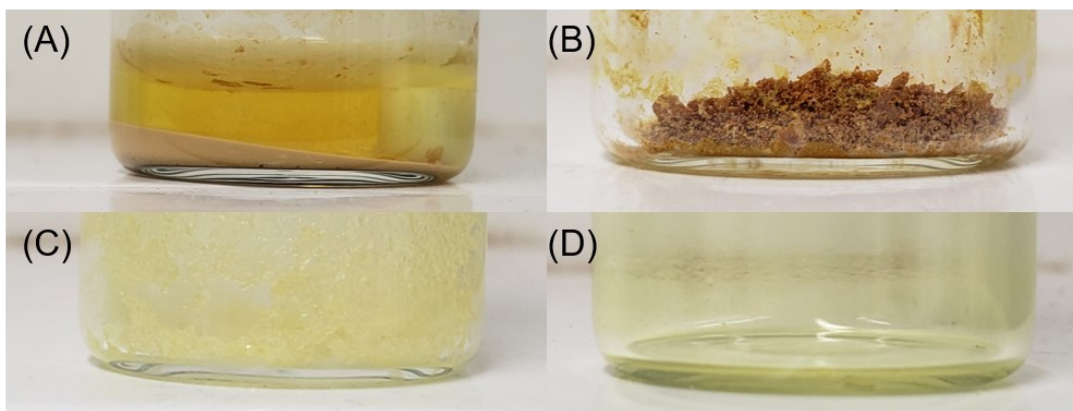
Fig.S15. Images of (A) final products of Diels-Alder polymer in pH 1 acetate buffer after 185 h of hydrolysis, (B) recollected bismaleimide in acetone fraction, (C) recollected pentaerythritol and bisphenol F in aqueous fraction, and (D) recollected HMF and maleic acid in ethyl acetate fraction.

Table S1. Recovery of monomers in each solvent fraction after 185 h hydrolysis of 6 wt% Diels-Alder polymer in pH 1 acetate buffer ([a]Diels-Alder polymer consists of ≥ tetramer, [b]Diels-Alder oligomers consist of ≤ tetramer, [c]Composition of Bisphenol F was analyzed by NMR spectrum of aqueous fraction; Free HMF, pentaerythritol, bismaleimide (BisMAL), and bisphenol F quantified the moles of each chemical in each solvent fraction; 'Maleic acid in BisMAL' and 'Bisphenol F in BisMAL' quantified the maleic acid units and bisphenol F units of the recovered bismaleimide).

|	Feed	Solid fraction	Theoretical monomer release	Monomers in Aqueous fraction	Monomers in EtOAc fraction	Monomers in Acetone fraction	Recovered monomers	Recovery (%)	Degradation (%)
[a]Diels-Alder polymer (g)	0.100	0.015	0.045	0.011	0.016	0.013	0.040	95.0	5.0
[b]Diels-Alder oligomer (g)	0	0.040							
Free HMF (mmol)	0.282	0	0.126	0.001	0.086	0	0.087	69.0	30.1
Free Pentaerythritol (mmol)	0.141	0	0.063	0.054	0.003	0	0.057	90.5	9.5
Free BisMAL (mmol)	0.141	0	0.063	0	0	0.037	0.037	58.7	41.3 (Hydrolysis)
Free Maleic acid (mmol)	0.282	0	0.126	0.004	0.042	0	0.046	95.2	4.8
Maleic acid in BisMAL (mmol)				0	0	0.074	0.074		
Free [c]Bisphenol F (mmol)	0.141	0	0.063	0.014	0	0	0.014	81.0	19.0
Bisphenol F in BisMAL (mmol)				0	0	0.037	0.037		

Table S2. Assumptions and parameters for calculating operating costs.

Variable operating cost	
Acetone purchase [$/kg][1]	0.7
Electricity purchase [$/kWh][2]	0.07
Water purchase [$/ton][2]	0.29
THF purchase [$/kg][3]	2
Isopropanol purchase [$/kg][4]	1.2
p-TSA purchase [$/kg][5]	45
NaHCO$_3$ purchase [$/kg][6]	0.2
HMF purchase [$/kg][7]	1.5
Pentaerythritol purchase [$/kg][8]	0.8
Bismaleimide purchase [$/kg][9]	6.5
Steam purchase [$/kJ][a]	2.50×10^{-6}
Cooling water purchase [$/kJ][a]	2.12×10^{-7}
Fixed operating cost	
Salaries [$/each operator/year][2]	65,000 × 6
Benefits and overhead [% of Salaries][2]	90
Maintenance [% of CAPEX][2]	3
Insurance [% of CAPEX][2]	0.7
Rent of land [% of ISBL + OSBL][3]	1

[a]Estimated from Aspen Economic Analyzer

Table S3. Assumptions and parameters for economic evaluation.

Lifetime [year]	20
Interest rate [%]	10
Income tax rate [%]	25
Depreciation method	Straight line
Plant operability per year [hours]	8,000

Table S4. Results of economic evaluation of the process for the Diels-Alder polymer production.

Total capital investment [thousands $]	**9,013.3**
ISBL	4,292.1
OSBL	1,716.8
Engineering	1,802.7
Contingency	1,201.8
Total operating cost [thousands $]	**6,470.0**
Fixed operating cost	1,144.4
Salaries	395.2
Benefits and overhead	355.7
Maintenance	270.4
Insurance	63.1
Rend of land	60.1
Variable operating cost	5,325.6
Electricity purchase	2.4
Steam purchase	3.0
Water purchase	0.17
THF purchase	2,208.2
Isopropanol purchase	461.4
p-TSA purchase	281.1
$NaHCO_3$ purchase	1.2
HMF purchase	389.6
Pentaerythritol purchase	112.2
Bismaleimide purchase	1,866.2

Table S5. Results of economic evaluation of the process for the bismaleimide recovery.

Total capital investment [thousands $]	**3,627.9**
ISBL	1,727.6
OSBL	691.0
Engineering	725.6
Contingency	483.7
Total operating cost [thousands $]	**996.0**
Fixed operating cost	909.2
Salaries	395.2
Benefits and overhead	355.7
Maintenance	108.8
Insurance	25.4
Rend of land	24.2
Variable operating cost	86.7
Electricity purchase	1.1
Steam purchase	58.0
Cooling purchase	6.9
Acetone purchase	20.6

Table S6. ISBL of major equipment units for the process for the Diels-Alder polymer production.

Equipment type	Equipment	Cost
Vessel	R-1	358,176
Vessel	R-2	3,240,604
Filter	F-1, F-2	253,033
Heater	H-1	57,777
Dryer	D-1, D-2	298,110
Pump[a]		95,368

[a] This process includes pumps to compensate for any small pressure or head losses between major unit processes.

Table S7. ISBL of major equipment units for the process for the bismaleimide recovery.

Equipment type	Equipment	Cost
Vessel	R-1	675,515
Vessel	R-2	76,082
Distillation column[a]	C-1	335,747
Storage tank	S-1, S-2	42,232
Filter	F-1, F-2	181,299
Cooler	C-1, C-2	24,953
Dryer	D-1, D-2	298,110
Pump[b]		93,654

[a] Distillation column includes tower, condenser and reboiler along with pump.
[b] This process includes pumps to compensate for any small pressure or head losses between major unit processes.

Supplementary References

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