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

| | |
|---|---|
| Journal: | *Green Chemistry* |
| Manuscript ID | GC-ART-08-2021-002865.R1 |
| Article Type: | Paper |
| Date Submitted by the Author: | 12-Sep-2021 |
| Complete List of Authors: | Chang, Hochan; University of Wisconsin Madison, Chemical and Biological Engineering<br>Kim, Min Soo; University of Wisconsin-Madison, Chemical and Biological Engineering<br>Huber, George; University of Wisconsin, Chemical and Biological Engineering<br>Dumesic, James; University of Wisconsin Madison, Chemical and Biological Engineering |
| | |

ARTICLE

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Hochan Chang[a], Min Soo Kim[a], George W. Huber[a], and James A. Dumesic[a,b]*

Acetalization of biomass-derived 5-hydroxymethyl furfural (HMF) with pentaerythritol produced a difuran (HPH) monomer in the presence of an acid catalyst. A recyclable polymer was then synthesized by Diels-Alder reaction of bismaleimide and the HMF-derived difuran (HPH). A polyurethane, produced from the Diels-Alder polymer has a higher glass transition temperature than a polyurethane, produced from ethylene glycol. The polyurethane, containing Diels-Alder polymer also has a self-healing ability. The Diels-Alder polymer could be hydrolyzed under acidic acetate buffer at 60℃ to produce the monomers for recycle. Each produced monomer was separated by solvent extraction, and the extracted monomers were recovered in different solvent fractions, such as aqueous, ethyl acetate, and acetone fractions. Techno economic analysis was used to assess the minimum selling price ($14.1 per kg) for the primary production of Diels-Alder polymer at a feed capacity of 400 ton per year. The economic viability of the primary recovery process for the most expensive recovered monomer, bismaleimide, was assessed by calculating the minimum selling price of the bismaleimide ($15.2 per kg). A circular closed-loop recycling production process for the Diels-Alder polymer was developed and this approach can produce the Diels-Alder polymer at $8.2 per kg when the feed capacity was 40 kton per year.

## Introduction

The increasing demands and uses of functional polymers have caused environmental concerns related to the disposal of waste polymers[1]. According to the MacArther foundation 40% of plastic wastes are sent to landfill, a third of plastics leak into the environment and 20% are burned, while only 14% are recycled with major losses during the recycling of the plastics[2]. Thus, development of new functional polymers that have unique properties for applications[3–5] and can be effectively recycled after their use[6] has attracted the interests of researchers and organizations. An ideal way to recycle the polymers is to fractionate the polymer into monomers and recover the monomers for various applications to synthesize other types of value-added commodity chemicals, including polymers[7], pharmaceutic ingredients[8], dyes[9], and liquid fuels[10]. Several key chemical challenges must be addressed to develop recyclable polymers[11]. First, the backbone of the polymers must contain reversible linkages to be broken to form oligomers or monomers. Second, fractionation of the polymers must be controllable under the target conditions. Third, the produced monomers by polymer fractionation must be effectively recovered. Reversible chemical linkages, such as Diels-Alder linkages[12] and cyclic acetal linkages[13], have been used to design recyclable polymers. To improve the amount of reversible bonding in the polymer backbone, a Diels-Alder polymer was developed by using a difuran and bismaleimide as monomers[14]. The difuran monomer from the previous work was synthesized by reaction of furfural and pentaerythritol. However, the use of furfural cannot provide additional chemical functionalities for further reactions and the scope of the study was limited to the synthesis and structure characterization of the Diels-Alder polymer without addressing the applications and recycling strategies. Acetalization of vanillin and glycerol synthesized a diol with a reversible cyclic acetal bond[13]. The diol was upgrade to the epoxy monomer and the monomer was cured by a diamine for production of a thermoset epoxy resin. The resin can by hydrolyzed under acidic conditions in acetone-water co-solvent. However, the monomers produced from the hydrolyzed polymer were degraded in the co-solvent and were not recovered for recycling. Therefore, it is important to develop a monomer that consists of controllable chemical functionality for polymerization and recycle at the target conditions.

5-hydroxymethyl furfural (HMF) is a biomass-derived chemical that can be (costs ~$1400 ton$^{-1}$) synthesized from corn starch[15]. HMF can be further upgraded to functional diols that produce performance-advantaged polymers[7]. Accordingly, HMF is a renewable platform chemical that can effectively converted to various monomers with useful chemical functionalities, such as furan, aldehyde, and hydroxyl groups. In this paper, we demonstrate the synthesis of a Diels-Alder polymer from HMF, pentaerythritol, and bismaleimide by acetalization and Diels-Alder reaction. The thermal properties and

---

[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*

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x self-healing ability produced by adding this Diels-Alder polymer to polyurethanes were investigated to demonstrate the application of the Diels-Alder polymer as a functional additive to polyurethanes. The Diels-Alder polymer can be fractionated to monomers and oligomers by hydrolysis under acidic conditions, and the produced monomers from the polymer can be recovered by solvent extraction. We also provide self-healing ability to a polyurethane by using the Diels-Alder polymer as a functional additive. The minimum selling price of Diels-Alder polymer and the economic feasibility of the monomer recovery process were assessed by techno economic analyses (TEA).

## Experimental methods

**Materials.** 5-hydroxymethyl furfural (HMF, AK Scientific, 98%), Pentaerythritol (Sigma-Aldrich, 99%), *p*-toluenesulfonic acid (*p*-TSA) monohydrate (Sigma-Aldrich, ≥98.5%), $NaHCO_3$ (Sigma-Aldrich, ≥99.7%), Bismaleimide (Sigma-Aldrich, 95%), Ethylene glycol (EG, Sigma-Aldrich, anhydrous, 99.8%), ,4'-methylenebis(phenyl isocyanate) (MDI, Sigma-Aldrich, 98%), Isopropanol (Sigma-Aldrich, for HPLC), 4Acetone (Fisher Scientific, HPLC grade), Tetrahydrofuran (THF, Sigma-Aldrich, 250 ppm BHT inhibitor, ≥99.0%), Dimethyl sulfoxide (DMSO, Sigma-Aldrich, anhydrous, ≥99.9%), 4-methyl-2-pentanone (MIBK, Sigma-Aldrich, HPLC grade), Ethyl acetate (EtOAc, Sigma-Aldrich, for HPLC, ≥99.7%), Acetic acid (Sigma-Aldrich, ≥99.7%), Hydrochloric acid (HCl, 6 N, Fisher Scientific), Sodium acetate (NaOAc, Sigma-Aldrich, >99%), Mill-Q water (MQ water, ~18 MΩ cm), Acetone-$d_6$ (ACROS organic, 99.8 atom% D, 0.03 % (v/v) TMS), Methanol-$d_4$ (ACROS organic, 99.8 atom% D, 0.03 % (v/v) TMS), DMSO-$d_6$ (Sigma-Aldrich, 99.9 atom% D, 0.03 % (v/v) TMS).

**Synthesis of HPH monomer.** HPH monomer was prepared by acetalization of HMF and pentaerythritol[16]. 5.0 g (39.7 mmol) of HMF and 2.7 g (19.8 mmol) of pentaerythritol were mixed in 35.5 g (45.1 mL) of isopropanol by a magnetic stirring bar. 0.08 g (0.4 mmol) of *p*-TSA monohydrate was added to the mixed solution in isopropanol to prepare the feed solution. The feed solution was stirred at room temperature (22-25°C) for 23 h. After 23 h of acetalization, HMF-derived difuran (HPH) was precipitated in isopropanol. 0.08 g (1 mmol) of $NaHCO_3$ was added into the product solution with HPH precipitates and stirred at room temperature for 30 min to neutralize *p*-TSA. HPH monomer was separated by vacuum paper filtration, and the monomer was washed by 20 mL of isopropanol, 10 mL of $NaHCO_3$ (100 mM) aqueous solution, and 20 mL of MQ water during the filtration. The washed HPH monomer was dried in vacuum oven (500-600 mbar, 50°C) for 2 days.

**Synthesis of Diels-Alder polymer.** 0.158 g (0.45 mmol) of HPH monomer and 0.162 g (0.45 mmol) of bismaleimide were mixed in 7 g (7.9 mL) of THF to prepare the feed solution. The feed solution was stirred at 50°C for 144 h to produce Diels-Alder polymer. During Diels-Alder reaction, 0.043g (50µL) of liquid aliquot was collected every day (~20-24 h) and diluted in 0.347 g (450µL) of acetone to prepare the HPLC sample for tracking the concentration of the unreacted HPH and bismaleimide. Diels-Alder polymer was separated from the liquid aliquot, containing the unreacted monomers and Diels-Alder oligomer, by centrifuge (5000 rpm, 5 min). The separated polymer was washed by 9 g of methanol and dried in under reduced pressure (200-50 mbar, 40°C) for 15 min.

**Hydrolysis of Diels-Alder polymer.** 3N HCl solution was prepared by diluting 6 N HCl solution in MQ water. pH 2 acetate buffer was prepared by mixing 0.115 g (1.40 mmol) of NaOAc, 0.046 g (0.76 mmol) of acetic acid, and 0.512 g of 3 N HCl in 16 g of water. pH 1 acetate buffer was prepared by mixing 0.115 g (1.40 mmol) of NaOAc, 0.051 g (0.84 mmol) of acetic acid, and 1.240 g of 3 N HCl in 16 g of water. The pH of the acetate buffers was measured with a pH meter. For hydrolysis under pH 2, 0.1 g of the polymer was dispersed in 1.5 g of pH 2 acetate buffer with a magnetic stirring bar and placed in an oil bath, set at 60°C. Similarly, 0.05 g of the polymer was dispersed in 3 g of pH 1 acetated buffer for hydrolysis under pH 1 condition and placed in an oil bath (60°C) with stirring. During hydrolysis, 0.1g (100µL) of liquid aliquot was collected every day (~20-24 h) and diluted in 0.399 g (400µL) of MQ water to prepare the HPLC sample for tracking the concentration of the produced monomer in aqueous phase.

**Addition of Diels-Alder polymer to polyurethanes.** MDI monomer provided urethane crosslinking between the backbones of Diels-Alder polymer by reacting with diol side groups of the Diels-Alder polymer to produce Diels-Alder polymer-MDI. For preparing the feed solutions, 0.21 g (0.86 mmol) of MDI was dissolved in 0.68 g (0.85 mL) of MIBK solvent, and 0.60 g (0.85 mmol of diol side group) of Diels-Alder polymer was dissolved in 0.94 g (0.86 mL) of DMSO solvent. MDI solution and Diels-Alder polymer solution were preheated for 9 min at 115°C and 80°C, respectively, to evaporate moisture in the feed solutions. The preheated solutions were mixed in a circular Al mold and cured at 80°C on a hot plate for 10 min. Then, the Al mold with the polymeric solution was placed into a vacuum oven (50°C, 500-600 mbar) for 19 h to evaporate DMSO and MIBK solvents.

Hydroxyl groups of the Diels-Alder polymer provided Diels-Alder crosslinking between the backbones of the polyurethane synthesized by EG and MDI to produce Diels-Alder polymer-EG-MDI. For preparing the feed solutions, 1.00 g (0.40 mmol) of MDI was dissolved in 1.28 g (1.6 mL) of MIBK solvent, and 0.10 g (0.14 mmol of diol side group) of Diels-Alder polymer and 0.24 (0.39 mmol) of EG were dissolved in 1.76 g (1.6 mL) of DMSO solvent. Both feed solutions were preheated at 115°C for 10 min. The preheated solutions were mixed in a circular Al mold and cured at 80°C on a hot plate for 20 min. Then, the Al mold with the polymeric solution was placed into a vacuum oven (50°C, 500-600 mbar) for 42 h to evaporate DMSO and MIBK solvents.

**Self-healing test of Diels-Alder polymer-EG-MDI.** Small pieces (e.g., 0.5-1 cm) of Diels-Alder polymer-EG-MDI were cut and placed on a glass dish. The cut pieces were pressurized under a metal rod (366 g) and placed on a hot plate at 130°C for 30 min. The polymer pieces with the metal rod were placed in a vacuum oven (50°C, 500-600 mbar) for 1 h. Then, the polymer pieces with the metal rod were cooled at room temperature (22-25°C) for 18 h.

**Recovery of Diels-Alder polymer by fractionation.** After 110-160 h of hydrolysis, the precipitates were separated from liquid aliquot by centrifuge (5000 rpm, 5 min). The bismaleimide and Diels-Alder oligomers produced by hydrolysis were selectively dissolved in THF fraction by adding 1 mL of THF to the separated precipitates, and the amount of bismaleimide was analyzed by HPLC. THF solvent was evaporated from the THF fraction under reduced pressure (<50 mbar, 40℃), and 0.65 g of acetone solvent was added to the dried THF fraction (solid) to selectively extract bismaleimide. The remaining solid was comprised of Diels-Alder oligomer. 6 g of EtOAc solvent and 0.6 g of saturated NaCl solution (brine) were added to the liquid aliquot for liquid-liquid extraction. The EtOAc fraction was separated from the aqueous fraction and 0.14 g of $MgSO_4$ was added to the EtOAc fraction to absorb the moisture. The residual solid fraction that has no solubility in THF, water, and EtOAc was comprised of Diels-Alder polymer. Each fraction was dried under reduced pressure (<50 mbar, 40℃) and characterized by NMR analysis.

**Techno economic analysis (TEA)**

The minimum selling price (MSP) of the Diels-Alder polymer produced and the recovered bismaleimide were calculated by techno economic analysis to assess the economic feasibility of the processes. We developed a process simulation model in Aspen Plus (V11 Aspen Technology) based on the experimental data. We carried out equipment sizing and cost analysis for the corresponding equipment based on the simulation results. The capital and operating costs of the distillation column, pumps and heat exchangers were estimated using Aspen Process Economic Analyzer (V11 Aspen Technology). The costs of the remaining equipment were estimated using engineering methods such as the proportional expression and the power law rules based on the cost data in the previous studies[17,18]. Tables S4 and S5 show the total capital investment and operating costs of the Diels-Alder polymer production and bismaleimide recovery processes, respectively. We then calculated MSPs of the Diels-Alder polymer from primary production, the bismaleimide recovered from our recycle method, and the Diels-Alder polymer from circular closed-loop recycling production. The capital and operating costs of the process were estimated by using economic parameters given in Tables S2 and S3. The MSPs were calculated to be $14.1 per kg of Diels-Alder polymer and $15.2 per kg of bismaleimide from primary production and recovery process, respectively, when the feed capacity was 400 ton per year. The Diels-Alder polymer production and bismaleimide recovery processes were integrated to develop a circular closed-loop recycling process, and the circular process was used to estimate the MSP of the Diels-Alder polymer with the recycled bismaleimide. The MSP of the circular Diels-Alder polymer was calculated to be $8.2 per kg at 40 kton per year of feed capacity.

**Primary production for Diels-Alder polymer.** We divided the Diels-Alder polymer production process into the HMF-derived difuran (HPH) monomer production section and Diels-Alder polymer production section, as shown in Figure 6(A). In HPH monomer production section, HMF and pentaerythritol are acetalized to HPH monomer (67 mol% yield[8]) by adding *p*-TSA monohydrate catalyst in isopropanol solvent. After the acetalization, *p*-TSA monohydrate is neutralized by $NaHCO_3$ and the resulting mixture is fed to the filter to obtain the solid phase of HPH monomer. The unreacted feeds (HMF, pentaerythritol) in isopropanol, along with generated water by-products, are recycled to acetalization reactor. The filtered HPH monomer is washed with water and then fed to the dryer. As a result, HMF and pentaerythritol are converted to purified HPH monomer in 48 mol% yield. In the Diels-Alder polymer production section, the purified HPH monomer and bismaleimide are mixed in THF solvent and fed to the Diels-Alder polymerization reactor, in which the temperature remains constant at 50℃. 54 wt% of Diels-Alder polymer is produced in the reactor and separated by vacuum filtration, while the remaining soluble portion, including HPH monomer, Diels-Alder oligomer, and bismaleimide in THF, is recycled to the Diels-Alder polymerization reactor. Finally, the Diels-Alder polymer produced is dried to remove residual THF solvent and then fed to the storage tank.

**Primary recovery process for bismaleimide.** A process block diagram of the bismaleimide recovery process that utilizes the Diels-Alder polymer as a feedstock was developed, as shown in Figure 7(A). Diels-Alder polymer in pH 1 acetate buffer enters the hydrolysis reactor, in which 26.7 wt% of Diels-Alder polymer is recovered in the aqueous phase as monomers (HMF, pentaerythritol, maleic acid, and bisphenol F), whereas 68.9 wt% of the mixture, containing bismaleimide, Diels-Alder oligomer and polymer, remains in the solid phase. The remaining 4.6 wt% of unknown by-products are purged and are labelled as degradation. The resulting product stream is then fed to the filter for liquid-solid separation. The solid phase stream, containing bismaleimide, Diels-Alder oligomer and polymer, is mixed in acetone and placed into a dissolution vessel. In the vessel, bismaleimide selectively dissolves in acetone, while the remaining solid portion includes Diels-Alder oligomer and polymer and is recycled to the hydrolysis reactor after passing through the dryer and cooler. The liquid solution from the filter is then sent to the distillation column to evaporate acetone, which is then cooled and recycled back to the bismaleimide dissolution vessel. The purity of the recovered bismaleimide from the distillation column is 99.1 wt %. Finally, the resulting bismaleimide is stored in a tank after removing acetone from the dryer.

**Circular closed-loop recycling production for Diels-Alder polymer.** Figure 7(A) shows a process diagram of a circular production process for Diels-Alder polymer in which the Diels-Alder polymer production and bismaleimide recovery processes were integrated. The recovered bismaleimide was used as one of the feeds in a production process for the Diels-Alder polymer. We assumed that the recycled bismaleimide was obtained from wastes sources of Diels-Alder polymer through four recycling steps including transport, collection, sorting, and recycling. The recycling cost for the waste Diels-Alder polymer was assumed to be $0.43/kg[19]. The production capacity of the recovery process for bismaleimide in the circular production process was designed to produce the required amount of bismaleimide for the production of the Diels-Alder polymer.

## Results and Discussion

### Synthesis and thermal properties of Diels-Alder polymer

Acetalization of HMF with pentaerythritol (HMF/Pentaerythritol (mol)=2) in isopropanol produced a biomass-derived diol (HPH) at room temperature (22-25℃) in the presence of *p*-toluenesulfonic acid (*p*-TSA)[16]. After 23 h of acetalization, HPH was precipitated in isopropanol due to its low solubility and the precipitated HPH was washed by isopropanol and water. The collected yield of HPH after drying was measured to be 48 mol% and was characterized by 2D HSQC NMR spectrum (Fig.S1). The upper yield of HPH has been reported to be 67 mol% based on thermodynamic equilibrium of acetalization[8]. The purified HPH was used as a diol feed for production of Diels-Alder polymer with bismaleimide. Equivalent molar amounts of HPH and bismaleimide were dissolved in tetrahydrofuran (THF) for Diels-Alder reaction without catalyst at 50℃ (Fig.1.(A)). The conversion of each monomer as a function of reaction time is showed in Fig.1.(B). 80 wt% of HPH and bismaleimide were converted to Diels-Alder adducts, including oligomers (26 wt%) and polymer (54 wt%). The oligomer was dissolved in THF solvent and the averaged-molecular weight of oligomers indicated that the oligomers consisted of dimer to tetramers by GPC analysis (Fig.S2).

Diels-Alder polymer, consisting of higher degree of polymerization (average DP=10), had no measurable solubility in THF, but did dissolve in DMSO-$d_6$ solvent for NMR analysis (Fig.S3). A DP of Diels-Alder polymer was calculated by quantifying the terminal maleimide moiety, terminal furan moiety, and Diels-Alder adduct bonds by $^{13}$C qNMR analysis. In Figure S3(B), the single chemical shift at 134.53 ppm with peak area of 0.40 represented 2 carbons of $HC_2{=}C_2H$ in terminal maleimide moieties. Similarly, 2 carbons of $HC_2{=}C_2H$ in terminal furan moieties were shown at 107.94 and 107.21 ppm with peak area of 0.40. 2 carbons of $HC_3$-$C_3H$ (red box in Fig.S3(C)) in Diels-Alder adduct bond were observed at 47.21-46.58 ppm with peak area of 4.00. The split chemical shifts at 47.21-46.58 ppm resulted from the endo- and exo-diastereoisomer[8]. The quantification of terminal groups and the bond formed in the Diels-Alder adduct calculated an average DP equal to 10.

ATR-FTIR spectra of Diels-Alder polymer, HPH monomer, and bismaleimide monomer are compared in Figure S4. The characteristic C-H and C-$H_2$ stretching were shown at 2870 cm$^{-1}$. C=O stretching in Diels-Alder adduct moiety was displayed in 1781 and 1704 cm$^{-1}$. The signals at 1641 and 1510 cm$^{-1}$ originated from C=C aromatic stretching in the Diels-Alder adduct moiety. Bands attributable to the C-N bond in the Diels-Alder adduct moiety were shown at 1383 and 1175 cm$^{-1}$. The cyclic acetal bonds were observed as bands at 1166 and 1083 cm$^{-1}$. Furthermore, the C-O-C moiety in the bridged 6-member ring of the Diels-Alder adduct was characterized at 1047 cm$^{-1}$. These characteristic ATR-FTIR signals are consistent with previous work[14] within 6 cm$^{-1}$ shift in wavenumber.

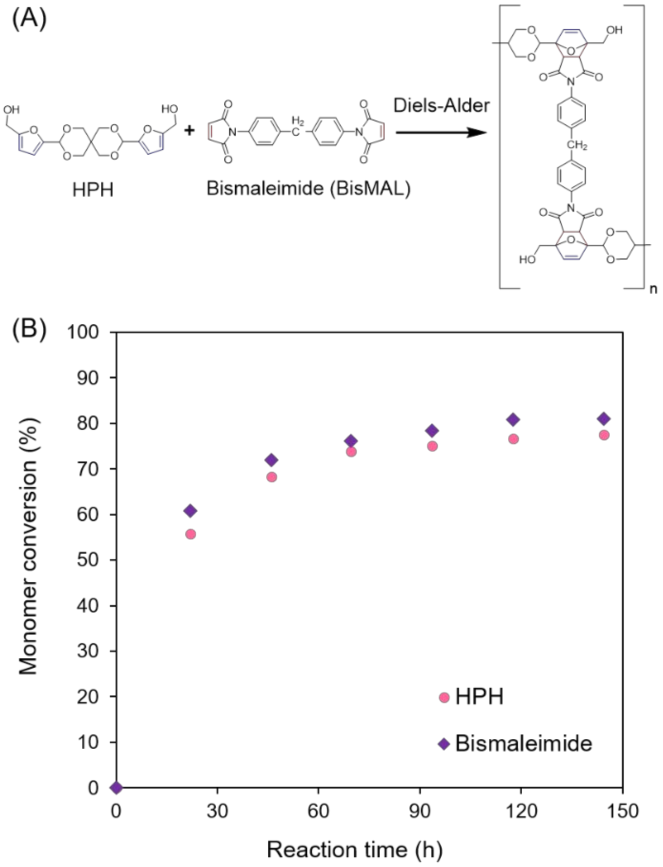

**Fig.1.** (A) Diels-Alder reaction pathway of HPH and bismaleimide for synthesis of Diels-Alder polymer, (B) Conversion of monomers by Diels-Alder reaction as a function of reaction time.

The thermal stability of the polymer was assessed by TGA analysis (Fig.S5.A). The polymer was thermally stable (<5wt % loss) up to 232℃ and underwent decomposition above 347℃. After heating to 700℃, 45 wt% of the polymer was converted to char. DSC analysis (Fig.S5.B) was used to measure the glass transition temperature ($T_g$) and the specific heat capacity ($C_p$). Based on 2nd cycle of heating and cooling cycle of DSC, the value of $T_g$ was measured to be 145℃. We note that the $C_p$ of glassy ($C_{p,glassy}$ = 1.5 J℃$^{-1}$g$^{-1}$ at <145℃) and rubbery polymer ($C_{p,rubbery}$ = 3.0 J℃$^{-1}$g$^{-1}$ at >145℃) were high. The difference between $C_p$ of the glassy and rubbery phase was 1.5 J℃$^{-1}$g$^{-1}$, compared to typical polyurethanes ($C_p$ = 0.6-0.9 J℃$^{-1}$g$^{-1}$)[7]. The significantly higher value of $C_p$ than polyurethanes and the large difference in $C_p$ between glassy and rubbery status can result from the reversible Diels-Alder linkages that are controlled by thermodynamic equilibrium, depending on temperature. The thermal stability, high $C_p$, and $C_p$ change of Diels-Alder polymer potentially enable applications for use as an advanced thermal insulator. For example, the $C_p$ of the polymer is tunable, depending on the operation temperature, and the rubbery phase $C_p$ (3.0 J℃$^{-1}$g$^{-1}$) is 3.3 times greater than typical polyurethanes (0.9 J℃$^{-1}$g$^{-1}$)[7] and can be used as a thermal insulator.

### Effect of Diels-Alder polymer addition on thermal properties of polyurethanes

The hydroxyl side groups of the Diels-Alder polymer enable the polymer (Fig.2.(B)) to be used as a polyol resource to synthesize polyurethanes by reacting with diisocyanates, such as 4'-

methylenebis(phenyl isocyanate) (MDI). We investigated the additive effect of the Diels-Alder polymer on the thermal properties of polyurethanes (Fig.2.(A)) by DSC analysis (Fig.S6). MDI can provide urethane crosslinking on the backbone of the Diels-Alder polymer by reacting with hydroxyl side groups of Diels-Alder polymer, thereby producing Diels-Alder polymer-MDI (74 wt% of Diels-Alder polymer in the polymer, Fig.2.(C)). Addition of the Diels-Alder polymer provides Diels-Alder crosslinking on the backbone of polyurethane (EG-MDI, Fig.2.(E)) to synthesize Diels-Alder polymer-EG-MDI (Diels-Alder polymer comprised 7.5 wt% of the blended polymer, Fig.2.(D)). 7.5 wt% addition of the Diels-Alder polymer to the polyurethane increases the $T_g$ from 79 to 142℃ and increased the difference between $C_p$ in glassy and rubbery phase of the polymer (Change in $C_p$) by 2.0 times (from 0.3 to 0.6 $J℃^{-1}g^{-1}$). These results indicate that the Diels-Alder polymer can be used as an additive to improve the thermal properties of polyurethanes.

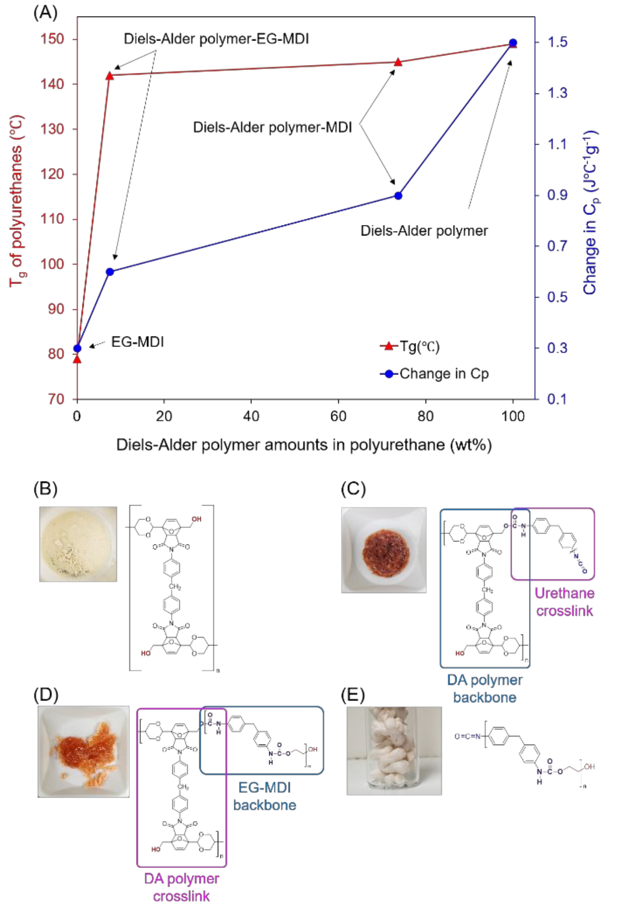

**Fig.2.** (A) $T_g$ and change in $C_p$ as a function of Diels-Alder polymer amounts (wt%) in polyurethane (Change in $C_p$ represents the $C_p$ difference between glassy and rubbery phase of polymers, Diels-Alder polymer amounts in polyurethane were calculated by weight of Diel-Alder polymer/weight of all monomers*100); Image and polymer structure of (B) Diels-Alder polymer, (C) Diels-Alder polymer-MDI, (D) Diels-Alder polymer-EG-MDI, and (D) EG-MDI polyurethane.

### Self-healing ability of polyurethane with Diels-Alder polymer additive

Diels-Alder linkages in a polymer structure can provide a self-healing ability to a polyurethane. Small pieces of cut Diels-Alder polymer-EG-MDI (Fig.3.(A)) were pressed under a weighted metal rod and heated on a hot plate at 130℃ for 30 min (Fig.3.(B)) to increase the mobility of the polymer chain by using retro Diels-Alder reaction. The heated and pressurized polymer pieces were placed in a vacuum oven (house vacuum, 500-600 mbar) at 50℃ for 1 h and cooled at room temperature for 18 h to regenerate Diels-Alder linkages. As a result of sequential pressurized heating and cooling processes, the cut pieces of polymers combined in one piece by self-healing (Fig.3.(C) and (D)).

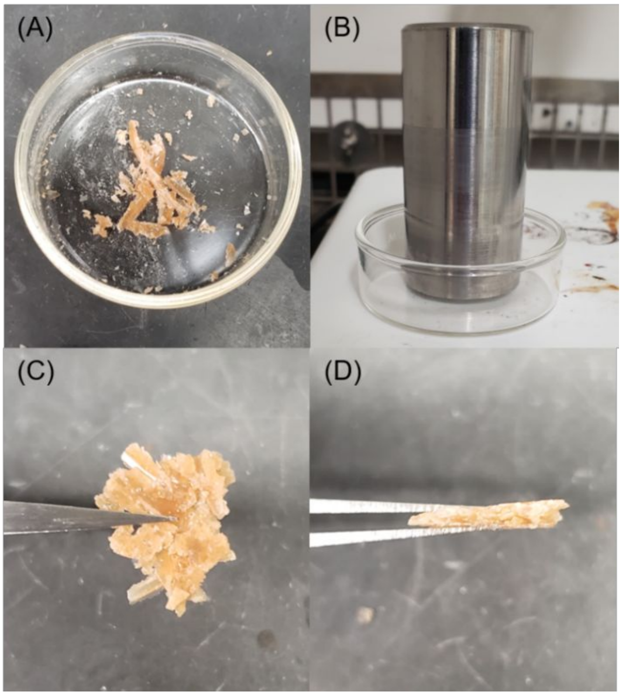

**Fig.3.** Images for (A) cut pieces of Diels-Alder polymer-EG-MDI, (B) the pressurized Diels-Alder polymer-EG-MDI on hot plate at 130℃, (C) top-view of self-healed Diels-Alder polymer-EG-MDI, and (D) side-view of self-healed Diels-Alder polymer-EG-MDI.

### Yield of monomers from Diels-Alder polymer by hydrolysis

Hydrolysis of cyclic acetals was used to a triggered retro Diels-Alder reaction[8] and resulted in the production of monomers from the Diels-Alder polymer (Fig.4.(A)). Moreover, retro Diels-Alder reactions are preferred to Diels-Alder reactions in the presence of Brønsted acids, such as HCl and acetic acid[20–22]. As a result, HPH units in Diels-Alder polymer were converted to HMF and pentaerythritol (Fig.S7.(A)) by hydrolysis and retro Diels-Alder reaction in acidic acetate buffer. Then, the cleavage of two HPH units enables the production of bismaleimide. An acidic acetate buffer was used to catalyze the hydrolysis and to prevent changes in the pH during the hydrolysis because hydrolysis of bismaleimide involves the production of $NH_4OH$ (Fig.S7.(B)). The yield of HMF and pentaerythritol is shown in Figure 4(B) and (C) under different pH conditions at 60℃. The initial rate of HMF formation was faster than that of pentaerythritol formation because the production of pentaerythritol is possible only if two HMF molecules are cleaved by hydrolysis. The molar ratio of the formed HMF to pentaerythritol converged to a value of 2.0 at longer reaction time (Fig.4.(D)). Similarly, the production of bismaleimide is possible only if two HPH units are cleaved by hydrolysis. Thus, the molar ratio of HMF derivatives (HMF, HMF hydrate, levulinic acid) to pentaerythritol to bismaleimide derivatives (bismaleimide, maleic acid, bisphenol F) converges 2:1:1 as hydrolysis of the polymer proceeds (HMF derivatives: Pentaerythritol: Bismaleimide derivatives (mol) = 2.0: 1.0: 0.6 and = 1.8: 1.0: 1.0 when conversion of the polymer reached 24 wt% and 45 wt%, respectively).

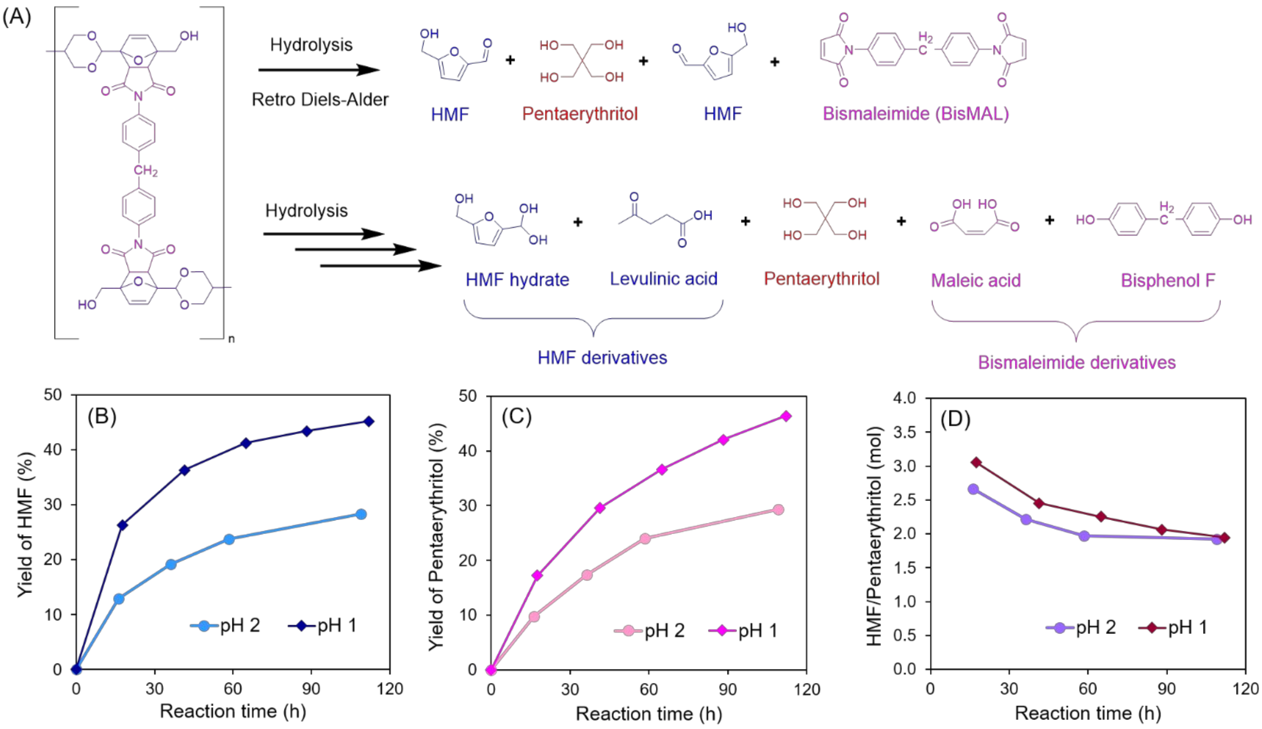

**Fig.4.** (A) Release mechanism of monomers by hydrolysis and retro Diels-Alder reaction pathways of Diels-Alder polymer; (B) Yield of HMF and (C) pentaerythritol by hydrolysis as a function of reaction time, (D) Molar ratio of HMF to pentaerythritol as a function of reaction time (Hydrolysis occurred at 60°C).

The effect of pH on the rate constant (*k*) of the polymer hydrolysis was investigated by tracking the amount of the produced HMF at constant temperature (60°C). A pseudo 2nd order reaction (Eq.1) was used to fit the kinetic model and the experimental data for polymer hydrolysis (Fig.S8). We note that a pseudo 1st order kinetic model cannot fit the experimental data and a pseudo 2nd order reaction was used to describe the hydrolysis at 60°C in a previous report[23]. The initial concentration of acid in acetate buffer and initial concentration of HPH unit in Diels-Alder polymer were represented as $[H^+]_0$ and $[HPH\ unit]_0$ in the kinetic model. At pH 1, the rate constant was calculated to be 21 ± 1.6 (95% confidential interval) $M^{-1}h^{-1}$ while it decreased to 12 ± 2.2 $M^{-1}h^{-1}$ at pH 2. Thus, the rate constant of hydrolysis of Diels-Alder polymer increased by 1.7 times as pH decreased from 2 to 1. The pH effect on the hydrolysis rate constant is consistent with our previous result of hydrolysis of the acetalized HMF (2.3 times increased by decreasing pH from 3 to 2 at 50°C)[8].

$$\text{(Eq.1)}\ \frac{d[HMF]}{dt} = k[H^+]_0[HPH\ unit]^2$$

$$([HPH\ unit]_0\ =\ [HPH\ unit] +\ [HMF])$$

**Recovery of the monomers produced by hydrolysis and fractionation**

A solvent-extraction recovery method has been reported to be an effective recycle method for multilayer plastic packaging materials[6]. The monomers produced from the Diels-Alder polymer, such as HMF, pentaerythritol, bismaleimide, maleic acid, and bisphenol F, have different solubilities in common green solvents[24], such as water, ethyl acetate (EtOAc), and acetone. Therefore, the solubility difference of each monomer enables a solvent-extraction recovery method to recycle the monomer produced by fractionation in common solvents (Fig.5). After 185 h of polymer hydrolysis, 45 wt% of the polymer was converted to monomers. HMF, pentaerythritol, maleic acid, and bisphenol F were dissolved in pH 1 aqueous phase, whereas bismaleimide, Diels-Alder oligomer, and polymer were precipitated as solid phase. HMF and maleic acid were extracted by EtOAc solvent from the aqueous solution (Fig.S9), while pentaerythritol and bisphenol F remained in the aqueous phase (Fig.S10). Bismaleimide was selectively extracted by acetone solvent from Diels-Alder oligomer and polymer (Fig.S11). Diels-Alder oligomers (40%) were extracted by THF solvent, and the THF-insoluble solid fraction (15%) was comprised of the Diels-Alder polymer (Fig.S12). The recovery of each monomer in each solvent fraction is summarized in Table S1. 95% of the Diels-Alder polymer was recovered as forms of monomers and Diels-Alder adducts (oligomer and polymer), with minor degradation (5%) during the hydrolysis and fractionation. The images of the recycled Diels-Alder polymer and the recollected monomers are shown in Fig.S15. HMF degradation (30.1%) was the major source of the degradation. 41.3% of bismaleimide was further hydrolyzed to maleic acid and bisphenol F (Fig.S7.(B)). 5% of the products (4.6 g per 100.3 g of DA polymer in Fig.5.) were degraded chemicals that were not detected by HPLC and NMR analysis and regarded as unknown by-products.

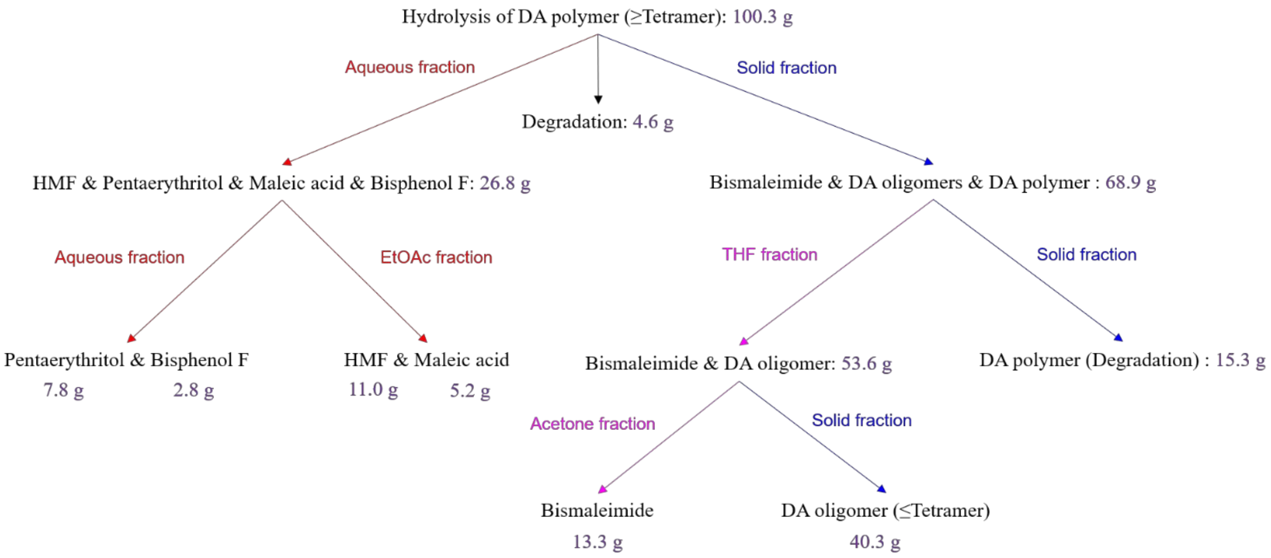

**Fig.5.** Fractionation of the produced monomers in common solvents

### Techno economic analysis (TEA)

#### Primary production of Diels-Alder polymer and recovery of bismaleimide

We simulated processes and carried out techno economic analysis (TEA) to assess the cost of Diels-Alder polymer and bismaleimide from primary production and recovery, respectively. The process diagrams, detailed methods and results of the model, along with economic assumptions and parameters are given in Figure S13 and Table S2-S7. The Diels-Alder polymer could be produced at a minimum selling price (MSP) of \$14.1/kg when the feed rate including HMF and pentaerythritol was 400 ton per year in Figure 6(A). The solvent and feedstock costs are the main cost drivers of the Diels-Alder polymer production process, accounting for 35.5% and 31.5% of the total annual required cost, respectively. Figure 6(B) showed the total ISBL cost and the MSP of the Diels-Alder polymer as a function of the feed capacity. The production cost (11.5-17.6 \$/kg) of Diels-Alder polymer was higher than the 5-year average price (4.5 \$/kg) of polyurethane.[19] The Diels-Alder polymer must thus have some properties advantages (higher glass transition temperature or self-healing ability) to justify this higher price.

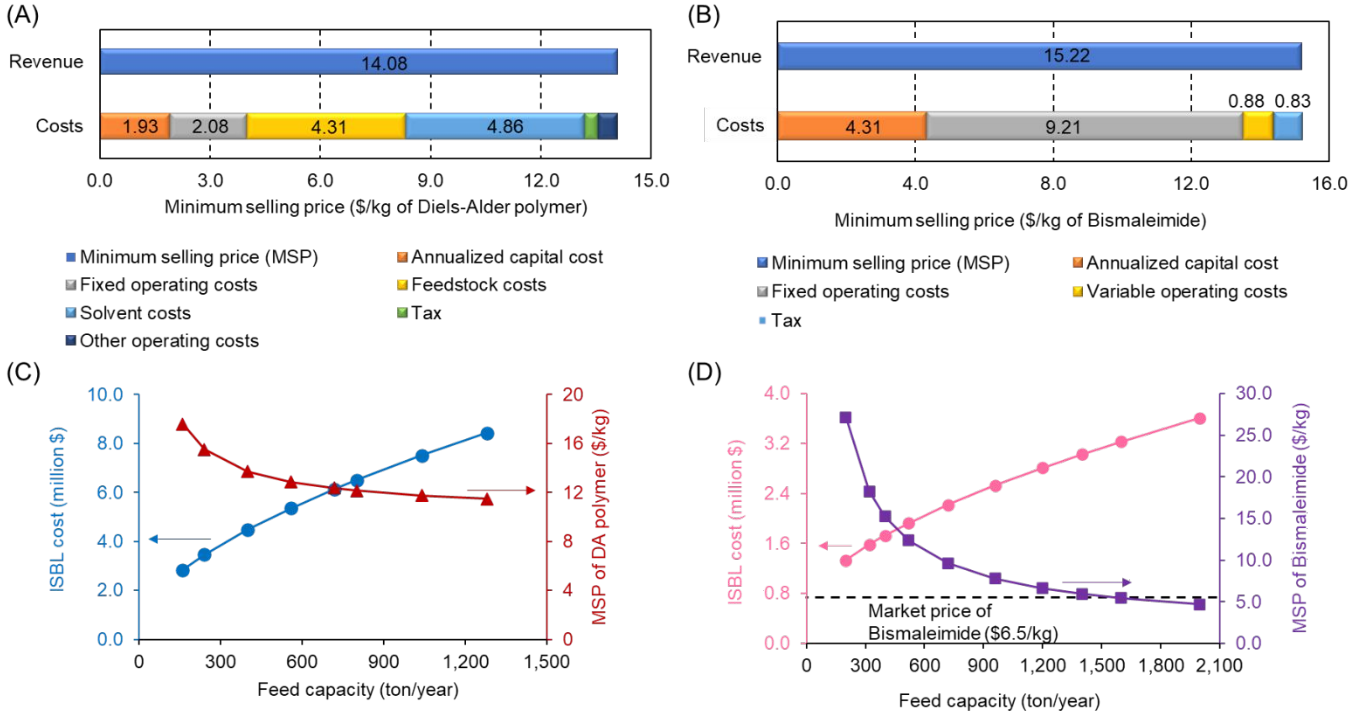

**Fig.6.** Cost breakdown of the primary (A) production for Diels-Alder polymer and (B) recovery for bismaleimide; Capital investment and minimum selling price (MSP) for (C) Diels-Alder polymer production and (D) for the bismaleimide recovery as a function of the feed capacity.

The economic viability of the recovery process was evaluated by performing TEA of the primary recovery process for bismaleimide based on the experimental data, because bismaleimide is the most expensive monomer. Figure S13(B) shows the flow diagram of the bismaleimide recovery process. The bismaleimide recovery process could produce 97.8 tons of bismaleimide per year at MSP of \$15.2 per kg by considering the Diels-Alder polymer feed rate of 400 ton per year (Fig.6.(C)). The ISBL cost of hydrolysis reactor (R-1) would be \$675,515 per year, about 39.1% of the total ISBL cost due to its high residence time and large usage of the acetate buffer as can be seen in Table S7. Figure 6(D) shows the total ISBL cost and the MSP of the bismaleimide recovery process as a function of the feed capacity of the Diels-Alder polymer. When the Diels-Alder polymer feed rate was 1,600 ton per year, the MSP of bismaleimide was \$5.4 per kg, which is about 16.3% less than the average market price of bismaleimide (\$6.5 per kg)[25].

### Circular closed-loop recycling production process of the Diels-Alder polymer

The circular production of the Diels-Alder polymer was developed[19] by integrating the production process of Diels-Alder polymer and recovery process of bismaleimide, as shown in Figure 7(A) Bismaleimide from the recovery process was used as feed for the production of Diels-Alder. Figure 7(B) shows the comparison of the MSPs of Diels-Alder polymer from the primary and circular process at the feed capacity, including HMF and pentaerythritol, of 40 kton per year. 116.3 kton per year of the Diels-Alder polymer waste was recycled for the production of recovered bismaleimide (28.7 kton per year). The recovered bismaleimide was converted to 54.9 kton per year of the Diels-Alder polymer in the circular process. The MSP of the Diels-Alder polymer from the circular process (\$10.15 per kg) was 19.5% lower than that from the primary process (\$8.2 per kg) in Figure 7(B). 19.5% was achieved due to the reduced cost of bismaleimide from circular production process (\$2.4 per kg in Fig.S14), compared to that from market price (\$6.5 per kg) from the primary production process.

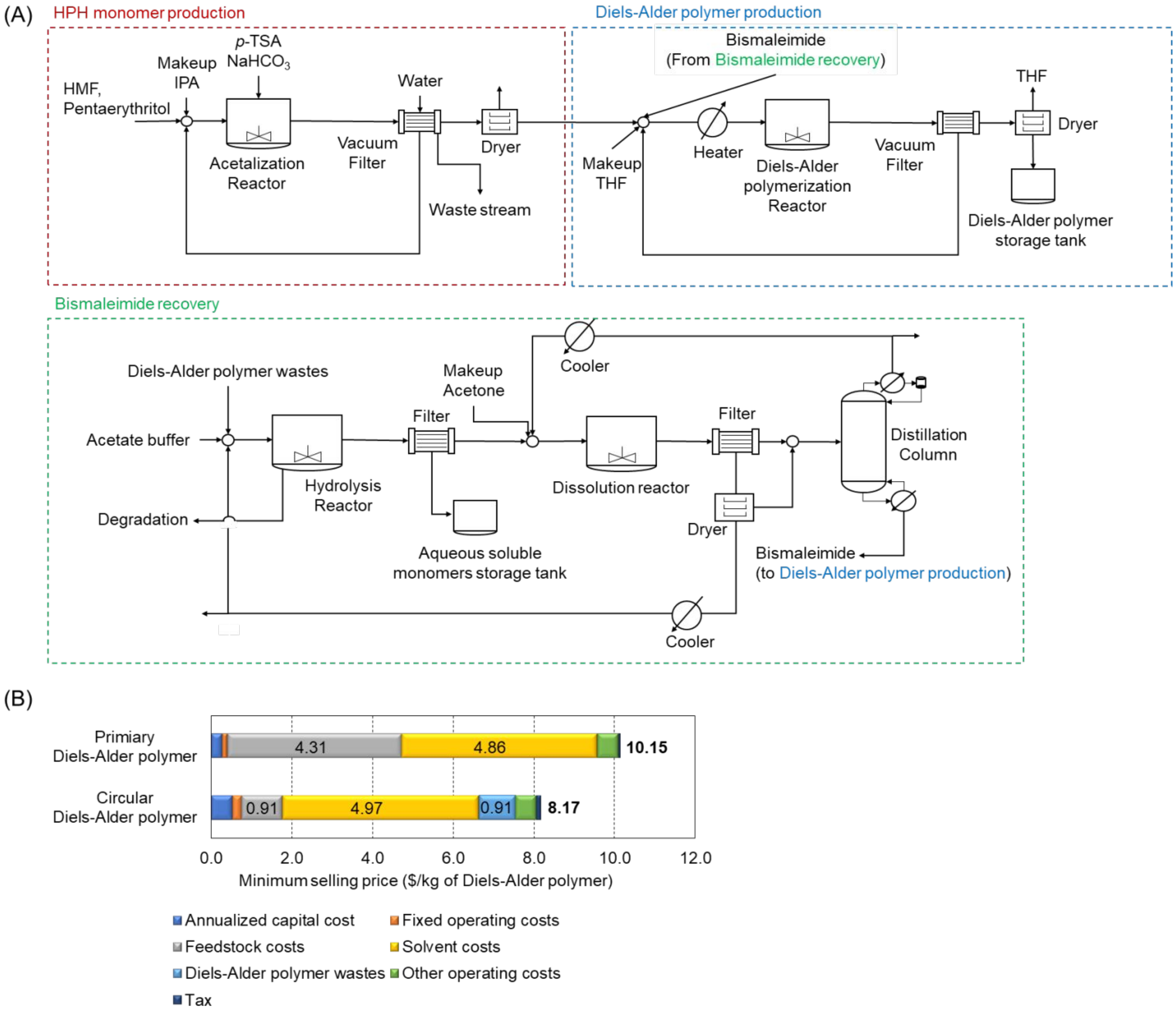

**Fig.7.** (A) Process flow diagram of the circular closed-loop recycling production of Diels-Alder polymer; (B) the minimum selling prices of the Diels-Alder polymer from the primary and circular production processes.

## Conclusion

HPH monomer, consisting of difuran and cyclic acetal groups, was synthesized by acetalization of HMF with pentaerythritol in the presence of *p*-TSA, and HPH was then used as a monomer for production of a closed-loop recycling polymer with bismaleimide by Diels-Alder reaction. The Diels-Alder polymer was thermally stable (<5 wt% loss at temperatures lower than 232°C) and behaved as a thermoplastic polymer with high $T_g$ (145°C) and $C_p$ (1.5-3.0 J°C$^{-1}$g$^{-1}$). The Diels-Alder linkages in the backbone of the polymer enabled a significant difference in the values of $C_p$ for the glassy (1.5 J°C$^{-1}$g$^{-1}$ at <145°C) and rubbery (3.0 J°C$^{-1}$g$^{-1}$ at >145°C) states of the polymer. Moreover, hydroxyl side groups of the Diels-Alder polymer enable the use of this polymer as an additive of polyurethanes to improve the thermal properties ($T_g$ and change in $C_p$) and provide self-healing ability. Therefore, the Diels-Alder polymer can be used as a functional additive for advantaged-polyurethanes, having self-healing abilities and improved thermal properties. Hydrolysis of the cyclic acetal bonds in HPH triggered the retro Diels-Alder reaction and produced monomers, such as HMF, pentaerythritol, and bismaleimide, from the Diels-Alder polymer under acidic (pH 1-2) acetate buffer. By decreasing the pH from 2 to 1, the rate of HMF formation increased by 1.7 times at constant temperature (60°C). The bismaleimide produced was further hydrolyzed to maleic acid and bisphenol F. These monomers produced by hydrolysis of the polymer were recovered by fractionation in different green solvents (Acetone, EtOAc, Water). We assessed the TEA for the production of Diels-Alder polymer. The MSP of the Diels-Alder polymer from the circular process was $8.2 per kg, which was 19.5% lower than the price from primary production when the feed capacity was 40 kton per year.

## Author Contributions

Hochan Chang contributed conceptualization, data curation, formal analysis, investigation, methodology, resources, validation, visualization, and writing; James A. Dumesic and George W. Huber contributed conceptualization, project administration, funding acquisition, supervision, and writing; Min Soo Kim contributed techno economic analysis and writing.

## Conflicts of interest

Authors declare that there is no conflict of interest.

## Acknowledgements

We thank the NMR facilities funded by: Thermo Q ExactiveTM Plus by NIH 1S10 OD020022-1; Bruker Quazar APEX2 and Bruker Avance-500 by a generous gift from Paul J. and Margaret M. Bender; Bruker Avance-600 by NIH S10 OK012245; Bruker Avance-400 by NSF CHE-414 1048642 and the University of Wisconsin-Madison; **Funding:** This material is based upon work supported in part by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division, under Contract DE-SC0014058 and the Great Lakes Bioenergy Research Center, U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research under Award Number DE-SC0018409. **Data and materials availability:** All data are available in the main text or the supplementary information.

## Notes and References

1 L. M. Heidbreder, I. Bablok, S. Drews and C. Menzel, *Sci. Total Environ.*, 2019, 668, 1077–1093.
2 *The New Plastics Economy: Rethinking the future of plastics | World Economic Forum*, 2016.
3 A. M. Diciccio and G. W. Coates, *J. Am. Chem. Soc.*, 2011, **133**, 10724–10727.
4 G. X. De Hoe, M. T. Zumstein, B. J. Tiegs, J. P. Brutman, K. McNeill, M. Sander, G. W. Coates and M. A. Hillmyer, *J. Am. Chem. Soc.*, 2018, **140**, 963–973.
5 N. A. Peppas and J. Klier, *J. Control. Release*, 1991, **16**, 203–214.
6 T. W. Walker, N. Frelka, Z. Shen, A. K. Chew, J. Banick, S. Grey, M. S. Kim, J. A. Dumesic, R. C. Van Lehn and G. W. Huber, *Sci. Adv.*, 2020, **6**, eaba7599.
7 H. Chang, E. B. Gilcher, G. W. Huber and J. A. Dumesic, *Green Chem.*, 2021, **23**, 4355–4364.
8 H. Chang, G. W. Huber and J. A. Dumesic, *ChemSusChem*, 2020, **13**, 5213–5219.
9 H. Chang, I. Bajaj, G. W. Huber, C. T. Maravelias and J. A. Dumesic, *Green Chem.*, 2020, **22**, 5285–5295.
10 H. Chang, A. H. Motagamwala, G. W. Huber and J. A. Dumesic, *Green Chem.*, 2019, **21**, 5532–5540.
11 B. D. Vogt, K. K. Stokes and S. K. Kumar, *ACS Appl. Polym. Mater.*, 2021, DOI:10.1021/ACSAPM.1C00648.
12 Y. Fang, X. Du, Y. Jiang, Z. Du, P. Pan, X. Cheng and H. Wang, *ACS Sustain. Chem. Eng.*, 2018, **6**, 14490–14500.
13 B. Wang, S. Ma, Q. Li, H. Zhang, J. Liu, R. Wang, Z. Chen, X. Xu, S. Wang, N. Lu, Y. Liu, S. Yan and J. Zhu, *Green Chem.*, 2020, **22**, 1275–1290.
14 C. Goussé and A. Gandini, *Polym. Int.*, 1999, **48**, 723–731.
15 H. Chang, I. Bajaj, A. H. Motagamwala, A. Somasundaram, G. W. Huber, C. T. Maravelias and J. A. Dumesic, *Green Chem.*, 2021, **23**, 3277–3288.
16 N. Warlin, M. N. Garcia Gonzalez, S. Mankar, N. G. Valsange, M. Sayed, S. H. Pyo, N. Rehnberg, S. Lundmark, R. Hatti-Kaul, P. Jannasch and B. Zhang, *Green Chem.*, 2019, **21**, 6667–6684.
17 P. Naviroj, J. Treacy and C. Urffer, *Sr. Des. Reports*.
18 R. E. Davis, N. J. Grundl, L. Tao, M. J. Biddy, E. C. Tan, G. T. Beckham, D. Humbird, D. N. Thompson and M. S. Roni, *Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels and Coproducts: 2018 Biochemical Design Case Update; Biochemical Deconstruction and Conversion of Biomass to Fuels and Products via Integrated Biorefinery Pathways*, Golden, CO (United States), 2018.
19 N. Vora, P. R. Christensen, J. Demarteau, N. R. Baral, J. D. Keasling, B. A. Helms and C. D. Scown, *Sci. Adv.*, 2021, **7**, eabf0187.

20 A. Maggiani, A. Tubul and P. Brun, *Chem. Commun.*, 1999, 2495–2496.
21 A. L. W. Demuynck, P. Levecque, A. Kidane, D. W. Gammon, E. Sickle, P. A. Jacobs, D. E. De Vos and B. F. Sels, *Adv. Synth. Catal.*, 2010, **352**, 3419–3430.
22 S. Kotha and S. Banerjee, *RSC Adv.*, 2013, **3**, 7642–7666.
23 L. Dandik and H. A. Aksoy, *J. Am. Oil Chem. Soc. 1992 6912*, 1992, **69**, 1239–1241.
24 D. Prat, A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehada and P. J. Dunn, *Green Chem.*, 2015, **18**, 288–296.
25 Bismaleimide Bismaleimide(bdm) Cas 13676-54-5 - Buy 13676-54-5,C21h14n2o4,Bismaleimide Bismaleimide(bdm) Product on Alibaba.com, https://www.alibaba.com/product-detail/bismaleimide-Bismaleimide-BDM-CAS-13676-54_60762843501.html?spm=a2700.galleryofferlist.normal_offer.d_title.58ef2756xFNITW, (accessed 25 February 2021).