Electronic Supplementary Material (ESI) for Polymer Chemistry. This journal is © The Royal Society of Chemistry 2018

Electronic Supplemental Information

### Synthesis, Characterization and Potential Applications of 5-Hydroxymethylfurfural Derivative Based Poly (β-thioether ester) Synthesized via Thiol-Michael Addition Polymerization

Daihui Zhang, Marie-Josée Dumont\*

Department of Bioresource Engineering, McGill University, 21111 Lakeshore Rd., Sainte-Anne-de-Bellevue, QC, Canada, H9X 3V9

\**Corresponding author and Page proof recipient:* 

Dr. Marie-Josée Dumont, PhD, P.Eng. Department of Bioresource Engineering McGill University, 21111 Lakeshore Rd., Sainte-Anne de Bellevue, Québec, Canada H9X 3V9 1-514-398-7776 marie-josee.dumont@mcgill.ca

### **1-Experimental Sections**

1.1-General procedure for the synthesis of TPEs

1.2-Diels-Alder reaction to crosslink TPEs

# **2-Results and Discussions**

# 2.1 Figures

**Figure S1.** <sup>1</sup>H NMR spectra of poly( $\beta$ -thioether ester) synthesized from A) DLdithiothreitol (92 % yield); B) 1,4-benzenedithiol (90 % yield)

**Figure S2.** <sup>13</sup>C NMR spectra of poly( $\beta$ -thioether ester) synthesized from A) 1,3-propanedithiol; B) dithiothreitol; C) 1,4-benzenedithiol

**Figure S3.** FTIR spectra of poly( $\beta$ -thioether ester) synthesized from a) 1,3-propanedithiol; b) dithiothreitol; c) 1,4-benzenedithiol

Figure S4. A) 5-methylfurfural generated at 250 °C and b) 1,6-hexanedithiol generated at 300 °C

**Figure S5.** DSC curves of poly( $\beta$ -thioether ester) synthesized from A) 1,3-propanedithiol; B) dithiothreitol; C) 1,4-benzenedithiol measured from -60 to 120 °C at heating rate of 10 °C/min, cooling rate of 5 °C/min

**Figure S6.** (A, B, C and D) DSC curves of copoly( $\beta$ -thioether ester) with varying monomer ratios; (E) T<sub>g</sub> evolution of copoly( $\beta$ -thioether ester) with varying benzene dithiol monomers. (Ratio 1:4 = the molar ratio of HS to BS)

Figure S7. TGA curves of copoly( $\beta$ -thioether ester) with different HS/BS feed ratios

**Figure S8.** (A) <sup>1</sup>H NMR spectra of DA reaction between BHF and bismaleimide at room temperature (the molar ratio of BHF to bismaleimide=2:1, CDCl<sub>3</sub> as solvent with a small amount of DMSO-d<sub>6</sub>); (B) Furan or maleimide conversion as a function of time; (C) Furan conversion *versus* reaction time at 25 °C and 40 °C, respectively

**Figure S9.** <sup>1</sup>H NMR spectra recorded at 110 °C in DMSO-d<sub>6</sub> for the retro DA reaction of furan-bearing poly( $\beta$ -thiother ester) and bismaleimide

**Figure S10.** (A) Strain-stress curves of crosslinked films (PHF/M 2:1) and film after compression molding; (B) FTIR of films before and after reprocessing; (C) DSC curve of crosslinked polymers (PHF/M 10:1)

Figure S11. SEM observations of film before (A) and after (B) reprocessing

Figure S12. FTIR spectra of TPEs synthesized via thiol-Michael addition polymerization

**Figure S13.** DSC curves of TPEs P1 (A), P2 (B), P3 (C), P4 (D) and P5 (E) synthesized from bio-based furan via thiol-Michael addition polymerization. Measured at heating rate of 10 °C/min, cooling rate of 5 °C/min

**Figure S14.** TGA curves of TPEs P1 (A), P2 (B), P3 (C), P4 (D), P5 (E)

**Figure S15.** DMA curves of TPEs: (A) Storage modulus vs. temperature, (B) Tan delta as a function of temperature

**Figure S16.** (A) FTIR of P2 and crosslinked P2-1 via Diels-Alder reaction (weight ratio of P2 to crosslinker = 10:1); (B) carbonyl peak regions

### 2.2 Tables

**Table S1.** GPC results of  $poly(\beta$ -thioether ester) prepared via different stoichiometric conditions

**Table S2.** Composition, thermal properties and molecular weights of synthesized copoly( $\beta$ -thioether esters)

**Table S3.** Polymerization conditions and molecular weights of TPEs

### 2.3 Schemes

Scheme S1. Synthesis of  $copoly(\beta-thioether ester)$  via the thiol-Michael addition polymerization

#### **1-Experimental Sections**

#### 1.1-General procedure for the synthesis of TPEs

In a typical procedure, 2,5-FDA (1.3 eq) was dissolved in THF (0.6 M). The solution was purged with nitrogen for 30 mins to remove oxygen. Thereafter, 1,3-propanedithiol (1 eq) was added via a syringe. The reaction mixture was cooled in an ice-bath. Then DMPP (0.005 eq) was added to the mixture to start the polymerization process. The reaction was carried out at room temperature for 15 mins. DL-dithiothreitol (0.3 eq) previously dissolved in THF was then added to the solution. The reaction was conducted for another 25 mins. Poly ( $\beta$ -thioether ester) was precipitated in cold hexane and recovered by filtration. Finally, the polymer was kept in a vacuum oven at room temperature overnight to remove residual solvent.

### **1.2-Diels-Alder reaction to crosslink TPEs**

Bismaleimide was used to crosslink 2,5-FDA based TPEs. A typical procedure is described as follows: 2,5-FDA based TPEs (0.5 g) were first dissolved in chloroform (3 mL), then bismaleimide (50 mg) was added. After TPEs and crosslinkers were dissolved completely, the solution was degassed and poured into a Teflon mold and sealed for 24 h to enable the DA reaction to occur. The solvent was completely evaporated in a vacuum oven at 40 °C for 24 h. The films were held at room temperature for at least 24 h before analysis.

#### **2-Results and Discussions**

#### 2.1 Figures



**Figure S1.** <sup>1</sup>H NMR spectra of poly( $\beta$ -thioether ester) synthesized from A) DLdithiothreitol (92 % yield); B) 1,4-benzenedithiol (90 % yield)

Signals (a, b) from  $\delta$ = 5.0 ppm to 6.5 ppm belonged to the furan protons and methylene protons next to the furan rings. Signals at  $\delta$ = 2.5 ppm to 3.0 ppm (c, d and e) represented the resonance from the methylene protons between the ester groups and the

thioether, and the protons adjacent to the thioether groups, respectively (Figure S1A, DMSO-d<sub>6</sub>). Moreover, two signals were observed at  $\delta = 3.5$ -3.6 ppm (f) and 4.6-4.8 ppm (g), being assigned to the protons of the hydroxyl groups and the protons next to the hydroxyl groups (POF). The signal from the protons of the benzene rings was observed at  $\delta = 7.2$ -7.3 ppm (e, Figure S1B, CDCl<sub>3</sub>, PBF).



**Figure S2.** <sup>13</sup>C NMR spectra of poly( $\beta$ -thioether ester) synthesized from A) 1,3-propanedithiol; B) dithiothreitol; C) 1,4-benzenedithiol



**Figure S3.** FTIR spectra of poly( $\beta$ -thioether ester) synthesized from a) 1,3-propanedithiol; b) dithiothreitol; c) 1,4-benzenedithiol

The ATR-FTIR spectra of different poly( $\beta$ -thioether ester) are presented in Figure S3. Characteristic bands, including C-H stretching vibrations at 3135 cm<sup>-1</sup>, the C=C ring stretching vibrations at 1565 cm<sup>-1</sup> and the ring vibration of the =C-O-C= groups at 1150 cm<sup>-1</sup>, were assigned to the furan rings. Carbonyl C=O stretching vibrations were observed at around 1730 cm<sup>-1</sup>. The bands at 2910–2950 and 2850–2860 cm<sup>-1</sup> were attributed to the asymmetric and symmetric stretching vibrations of the CH<sub>2</sub> groups, respectively.



**Figure S4.** A) 5-methylfurfural generated at 250 °C and B) 1,6-hexanedithiol generated at 300 °C



**Figure S5.** DSC curves of poly( $\beta$ -thioether ester) synthesized from A) 1,3-propanedithiol; B) dithiothreitol; C) 1,4-benzenedithiol measured from -60 to 120 °C at a heating rate of 10 °C/min, a cooling rate of 5 °C/min



**Figure S6.** (A, B, C and D) DSC curves of copoly( $\beta$ -thioether ester) with varying monomer ratios; (E) T<sub>g</sub> evolution of copoly( $\beta$ -thioether ester) with varying benzene dithiol monomers. (Ratio 1:4 = the molar ratio of HS to BS)



Figure S7. TGA curves of copoly( $\beta$ -thioether ester) with different HS/BS feed ratios





**Figure S8.** (A) <sup>1</sup>H NMR spectra of DA reaction between BHF and bismaleimide at room temperature (the molar ratio of BHF to bismaleimide=2:1, CDCl<sub>3</sub> as solvent with a small amount of DMSO-d<sub>6</sub>); (B) Furan or maleimide conversion as a function of time; (C) Furan conversion *versus* reaction time at 25 °C and 40 °C, respectively



**Figure S9.** <sup>1</sup>H NMR spectra recorded at 110 °C in DMSO-d<sub>6</sub> for the retro DA reaction of furan-bearing poly( $\beta$ -thiother ester) and bismaleimide



**Figure S10.** (A) Strain-stress curves of crosslinked films (PHF/M 2:1) and film after compression molding; (B) FTIR of films before and after reprocessing; (C) DSC curve of crosslinked polymers (PHF/M 10:1)



Figure S11. SEM observations of film before (A) and after (B) reprocessing.



Figure S12. FTIR spectra of TPEs synthesized via thiol-Michael addition polymerization

The ATR-FTIR spectra of TPEs are presented in Figure S12. Characteristic bands, such as C-H stretching vibrations at 3135 cm<sup>-1</sup> and the ring vibration of the =C-O-C= groups at 1150 cm<sup>-1</sup>, were assigned to the furan rings. Carbonyl C=O stretching vibrations were observed at around 1730 cm<sup>-1</sup>. The bands at 2910–2950 and 2850–2860 cm<sup>-1</sup> were assigned to the asymmetric and symmetric stretching vibrations of the CH<sub>2</sub> groups, respectively. Furthermore, a broad O-H stretching absorption band (3400 cm<sup>-1</sup>) was observed in all samples. While the presence of interactions between carbonyl groups and the hydroxyl groups leading to the shift of carbonyl stretching vibrations to a lower wavenumber has been observed in the POF, this observation was not confirmed here probably due to the low intensity of the shifted signal.



**Figure S13.** DSC curves of TPEs P1 (A), P2 (B), P3 (C), P4 (D) and P5 (E) synthesized from bio-based furan via thiol-Michael addition polymerization. Measured at a heating rate of 10 °C/min, a cooling rate of 5 °C/min



**Figure S14.** TGA curves of TPEs P1 (A), P2 (B), P3 (C), P4 (D), P5 (E)



**Figure S15.** DMA curves of TPEs: (A) Storage modulus vs. temperature, (B) Tan delta as a function of temperature



**Figure S16.** (A) FTIR of P2 and crosslinked P2-1 via Diels-Alder reaction (weight ratio of P2 to crosslinker = 10:1); (B) carbonyl peak regions

# 2.2 Tables

Table S1. GPC results of  $poly(\beta$ -thioether ester) prepared via different stoichiometric conditions

Acrylate: Thiols <sup>a</sup>	M <sub>n</sub> (g/mol) <sup>b</sup>	PDI
1.2:1	3466	2.8
1.1:1	14806	1.9
1:1	21834	2.0
1:1.1	10008	2.0
1:1.2	2803	2.1

<sup>a</sup> The ratio of 2,5-FDA and 1,3-propanedithiol. <sup>b</sup> Polystyrene as standard.

	<sup>1</sup> H NMR <sup>1</sup> H NMR HS/BS ratio (mol%)	GPC		DSC				TGA
Polymers		Molecular weight (M <sub>n</sub> *10 <sup>3</sup> g/mol) <sup>a</sup>	PDI	First Heating		Second Heating		
				Tg (⁰C) <sup>b</sup>	Т <sub>т</sub> (°С) <sup>г</sup>	T <sub>g</sub> (⁰C)	T <sub>m</sub> (°C) d	T5%(°C) <sup>c</sup> , T <sub>max</sub> (°C) <sup>e</sup>
PHF <sup>j</sup>	5/0	19.5	2.0	#	56.1/77.4	- 36.9	#	236, 249/285
PHF/PBF- 4:1	4.2/0.8	14.7	1.7	-27.1	54.0/69.5	- 30.1	#	249, 254/291
PHF/PBF- 3:2	3.2/0.8	16.4	1.7	-20.8	47.6	- 23.2	#	243, 252/292
PHF/PBF- 2:3	1.9/3.1	17.0	1.6	-18.5	49.3/53.7	- 16.3	#	236, 247/291
PHF/PBF- 1:4	0.9/4.1	13.5	1.8	-6.4	49/56.0/77.5	-5.3	#	236, 246/289
PBF	0/5	17.8	1.9	8.0	64.0/80.6	7.9	#	242, 246/292

**Table S2.** Composition, thermal properties and molecular weights of synthesized copoly( $\beta$ -thioether esters)

<sup>a</sup> Polystyrene as standard. <sup>b</sup> Glass transition temperature. <sup>c</sup>  $T_{5\%}$  indicates the 5% weight loss of polymers under a nitrogen atmosphere. <sup>d</sup> Melting temperature. <sup>e</sup>  $T_{max}$  indicates the temperature of maximal rate of decompositions. <sup>f</sup> Multiple melting temperature. # = not detected. <sup>j</sup> Polymers synthesized from 1,6-hexanedithiols.<sup>6b</sup>

Sample s	P/D <sup>a</sup>	P/D <sup>b</sup>	M <sub>n</sub> (kg/mol) <sup>c</sup>	PDI	T <sub>g</sub> (°C) <sup>d</sup>	T <sub>5%</sub> (°C) <sup>e</sup> , T <sub>max</sub> (°C) <sup>f</sup>
P1	10/3	10/3.1	20.5	2.0	-22.0	245, 249/282
P2	10/4	10/3.8	19.2	2.1	-20.1	242, 247/280
Р3	10/5	10/4.8	16.9	2.0	-19.1	242, 246/277
P4	10/5	10/4.5	13.0	2.3	-22.6	242, 247/280
P5	10/7	10/6.2	13.9	2.6	-16.1	238, 242/277

Table S3. Polymerization conditions and molecular weights of TPEs

<sup>a</sup> The feeding molar ratio of 1,3-propanedithiol to dithiothreitol. <sup>b</sup> The molar ratio of 1,3-propanedithiol to dithiothreitol determined via <sup>1</sup>H NMR spectra. <sup>c</sup> The number average molecular weight and PDI ( $M_w/M_n$ ) determined by GPC calibrated with polystyrene. <sup>d</sup> Glass transition temperature. <sup>e</sup> T<sub>5%</sub> indicates the 5% weight loss of polymers under a nitrogen atmosphere. <sup>f</sup> T<sub>max</sub> indicates the temperature of maximal rate of decompositions.

# 2.3 Schemes



Scheme S1. Synthesis of copoly( $\beta$ -thioether ester) via the thiol-Michael addition polymerization