

## Supporting Information

### **Copolymers of Tetrahydrofuran and Epoxidized Vegetable Oils: Application to Elastomeric Polyurethanes**

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### **Wet chemical analysis of product**

All wet chemical analyses were performed according to the AOCS official methods (*Official Methods and Recommended Practices of the American Oil Chemists' Society, Acid Value (Te 1a-64), Hydroxyl Value (Cd 13-60); Oxirane Content (Cd9-57);* 6<sup>th</sup> Ed. 2009, AOCS Press, Illinois, USA.) acid value (AV), Te 1a-64 (89); hydroxyl value (OHV), Cd 13-60(89).

#### Procedure for acid value analysis:

- (a) Weigh 0.5 g of sample into an Erlenmeyer flask.
- (b) Add approximately 100 ml of neutralized solvent (Isopropanol : Toluene, 50:50 mixture) and 3 drops of indicator (1% phenolphthalein in methanol)
- (c) Mix until sample completely dissolved.
- (d) Titrate with standardized alkali solution (0.1 N KOH in ethanol), stirring vigorously to the appearance of the first permanent pink color that persist for 1 minute.

Calculation : Acid value, mg KOH per gram of sample =

$$\frac{\text{volume of alkali, mL} \times N \times 56.1}{\text{mass of sample, g}}$$

where N = normality of alkali determined by standardization.

Procedure for hydroxyl value analysis:

- (a) Weigh 1.0 g of sample into an Erlenmeyer flask.
- (b) Pipet 5.0 ml of pyridine-acetic anhydride reagent (pyridine : acetic anhydride, 3:1) into the flask containing the sample for acetylation. Thoroughly mix the contents by gentle swirling.
- (c) Pipet 5.0 ml of pyridine-acetic anhydride reagent into an empty flask for the reagent blank.
- (d) Place the samples and blank flasks on a hot plate, under a reflux condenser and heat at 100 °C for 1 hour.
- (e) Add 10 ml of water through the condenser to the flask and heat for an additional 10 minute with the reflux condenser attached.
- (f) Allow the flask to cool to room temperature with condenser attached.
- (g) Using a total of about 25 ml of neutralized butyl alcohol, wash the condenser with about 12 ml, remove the condenser and use the remaining butyl alcohol to wash the sides of the flask.
- (h) Add 1 ml of phenolphthalein indicator solution. Titrate to a faint pink end point with 0.5 N alcoholic KOH solution.

Calculation : The hydroxyl value is calculated as follow:

$$\text{Hydroxyl Value} = \frac{B - S \times N \times 56.1}{W}$$

Where

B = volume, ml KOH solution required for the reagent blank

S = volume, ml KOH solution required for titration of the acetylated sample

N = normality of alcoholic KOH determined by standardization

W = mass, gram of sample used for acetylation

## Characterization

Infrared spectra were recorded as solid or liquid on Perkin-Elmer Spectrum100 FTIR spectrometer and absorption maxima ( $\nu_{\max}$ ) are recorded in wavenumbers ( $\text{cm}^{-1}$ ). Solids were compressed into a thin table and non-volatile liquids were analyzed as thin film over diamond ATR top plate. High resolution mass spectrometry was achieved by using BrukerMaXis instrument to carry out accurate ESI mass analysis.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy were recorded on Bruker DPX-400 at 400 MHz and 100 MHz respectively at 298K with approximately 10% w/v solutions in deuterated NMR solvents. Chemical shifts are quoted in ppm relatively to internal standard tetramethylsilane (TMS) and reference to the residual solvent. All coupling constant are quoted in hertz (Hz). MALDI-TOF-MS measurement was performed with a BrukerDaltonicsUltraflex II TOF/TOF mass spectrometer equipped with a nitrogen laser delivering 3-ns laser pulses at 337 nm. 5 mg of sample was dissolved in 100  $\mu\text{l}$  tetrahydrofuran and 50 mg of 2,5-dihydroxybenzoic acid (DHB) as the matrix was dissolved in 200  $\mu\text{l}$  tetrahydrofuran. Sample solution (5  $\mu\text{l}$ ) and matrix solution (20  $\mu\text{l}$ ) were mixed and 0.5  $\mu\text{l}$  of this mixture was spotted on the target plate and analyzed. The sample was irradiated with 300-600 pulsed laser shots at a 20% laser power and was measured in reflectron ion mode and was calibrated against poly (ethylene glycol) methyl ether. GPC with THF as the eluent was performed on an Agilent 390-MDS that has an autosampler and a PLgel 5.0  $\mu\text{m}$  bead-size guard column (50  $\times$  7.5 mm), followed by two linear 5.0  $\mu\text{m}$  bead-size PLgel Mixed D columns (300  $\times$  7.5 mm) and a differential refractive index detector. Analysis was performed using THF (2% v/v TEA) as the eluent at 30  $^{\circ}\text{C}$  with a flow rate of 1  $\text{mL min}^{-1}$ . The GPC system was calibrated using linear poly(methyl methacrylate) EasiVial standards (Agilent Ltd.) range from 200 to  $10^5$  Da and polystyrene EasiVial standards (Agilent Ltd.) range from 162 to  $10^5$  Da. Data were collected and analyzed using Cirrus GPC/SEC software (version 3.3).

### Screening of Lewis Acids as potential catalysts

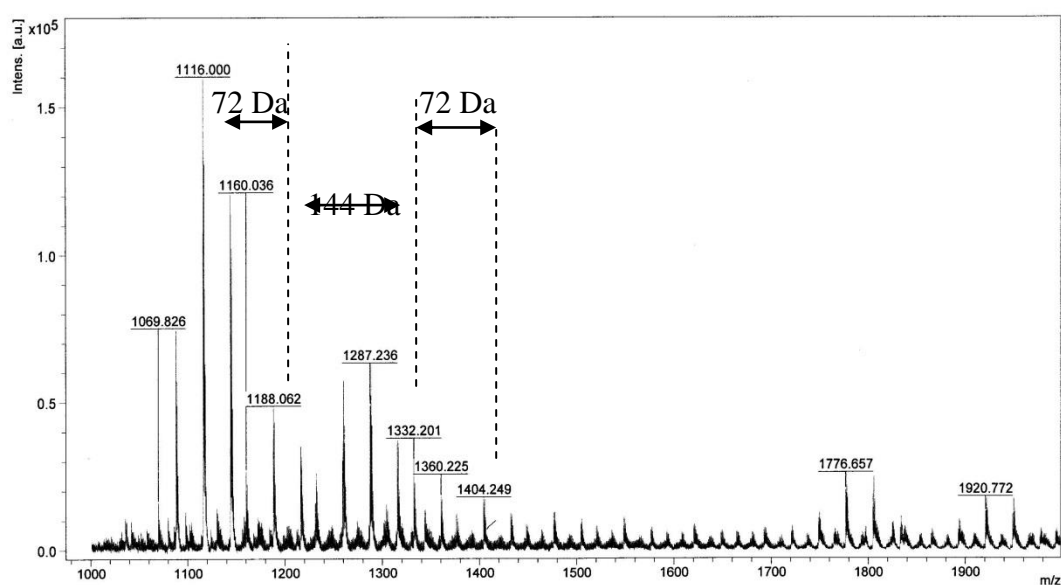
Chemical compound	Mol equivalent of chemical	Polymer content (%)	Gel permeation chromatography		
			M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI
BF <sub>3</sub> .EtO <sub>2</sub>	0.02	97	282K	56K	6.4
FeCl <sub>3</sub>	0.1	90	45K	17K	2.6
SnCl <sub>4</sub>	0.1	93	111K	25K	4.4
AlCl <sub>3</sub>	0.1	0	-	-	-
TiCl <sub>4</sub>	0.1	0	-	-	-
HBF <sub>4</sub>	0.02	95	85K	22K	3.8
CF <sub>3</sub> SO <sub>3</sub> H	0.1	92	165K	36K	4.6
ClSO <sub>3</sub> H	0.1	0	-	-	-
CF <sub>3</sub> CO <sub>2</sub> H	0.1	0	-	-	-
H <sub>2</sub> SO <sub>4</sub>	0.1	0	-	-	-

M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index

## General procedure for formation of p(THF-EVO) with $\text{BF}_3 \cdot \text{OEt}_2$ .

### Synthesis of p(THF-ECB) as an example

Epoxidized cocoa butter (50 g, 57 mmol) was added to dry tetrahydrofuran (250 mL) and the mixture stirred at 20 °C under  $\text{N}_2$  atmosphere for 30 minutes.  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.81 g, 5.7 mmol) was added drop-wise and the mixture stirred for a further 24 hours at 20 °C. To the crude reaction was added saturated NaCl solution (200 mL) and chloroform (300 mL). The organic layer was washed with saturated  $\text{NaHCO}_3$  solution (100 mL), saturated NaCl solution (200 mL) and dried over anhydrous  $\text{MgSO}_4$ . Removal of solvent *in vacuo* yielded a clear viscous liquid (120 g).  $\nu_{\text{max}}/\text{cm}^{-1}$  3360 (O-H) 2921, 2850 (C-H) 1742 (C=O) 1105 (C-O) 754 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 5.24\text{-}5.28$  (1H, m,  $\text{CHO}$ ) 4.25 (2H, dd,  $J = 11.9$  Hz, 4.4 Hz,  $\text{CH}_2\text{O}$ ), 4.10 (2H, dd,  $J = 11.9$  Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.43 – 3.30 (64H, m,  $\text{HCO}$ ), 2.26 (6H, t,  $J = 7.5$  Hz,  $\text{O=CCH}_2\text{CH}_2$ ), 1.62-1.50 (72H, m,  $\text{O=CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.30-1.18 (72H, m,  $\text{CH}_2\text{CH}_2$ ), 0.83 (9H, t,  $J = 6.8$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 173.2$ , 172.8 (C=O) 70.4 ( $\text{HC-O}$ ) 68.9 ( $\text{HC-O}$ ), 62.0, 61.8 ( $\text{H}_2\text{C-O}$ ), 33.9 ( $\text{O=CCH}_2$ ), 26.3 ( $\text{O=CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 29.5, 22.4 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.9 ( $\text{CH}_2\text{CH}_3$ ).

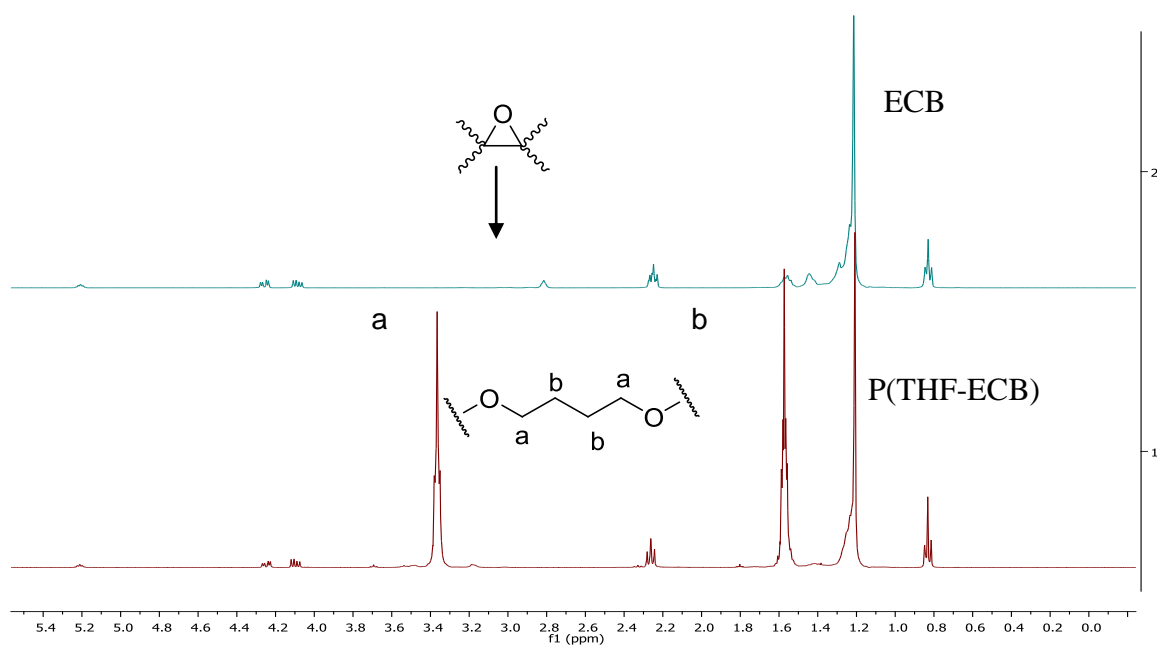


MALDI-TOF-MS spectrum of p(THF-ECB) by using DHB as the matrix in the analysis

### Properties of p(THF-ECB)

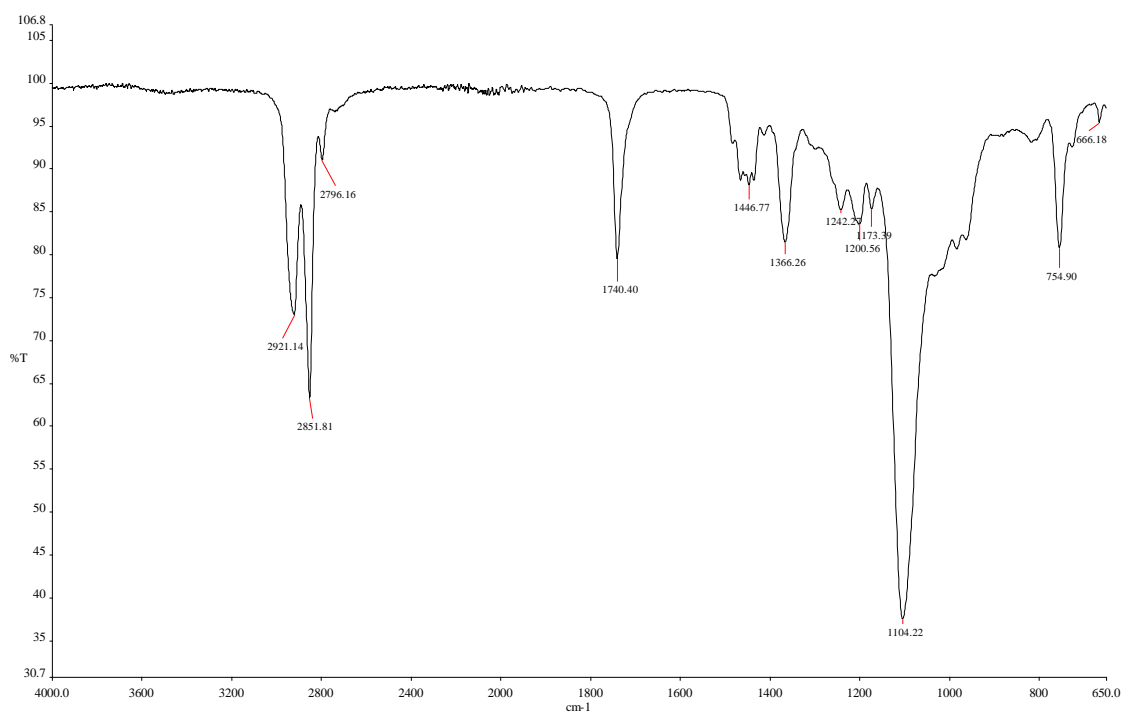
Entry	Mol equivalent of BF <sub>3</sub> .Et <sub>2</sub> O	Yield (%)	Gel permeation chromatography		
			M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI
1	0.02	0	-	-	-
2	0.05	82	37K	16K	2.3
3	0.1	93	83K	30K	2.8

M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index

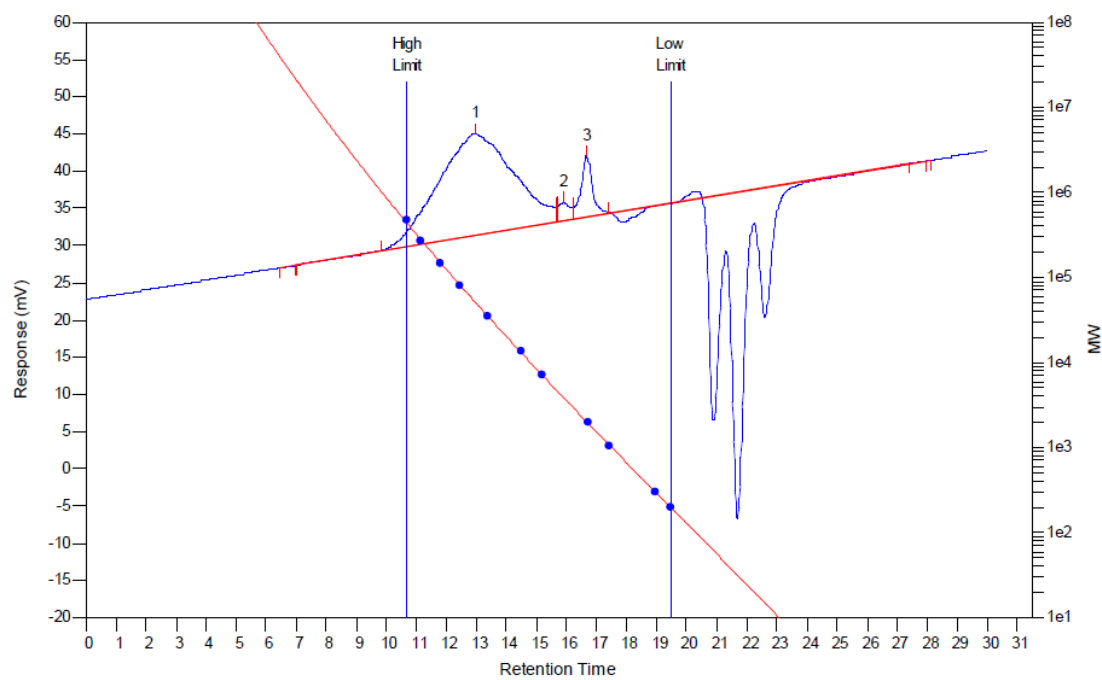


Stacked 400 MHz <sup>1</sup>H NMR spectrum of ECB and p(THF-ECB) in CDCl<sub>3</sub>.





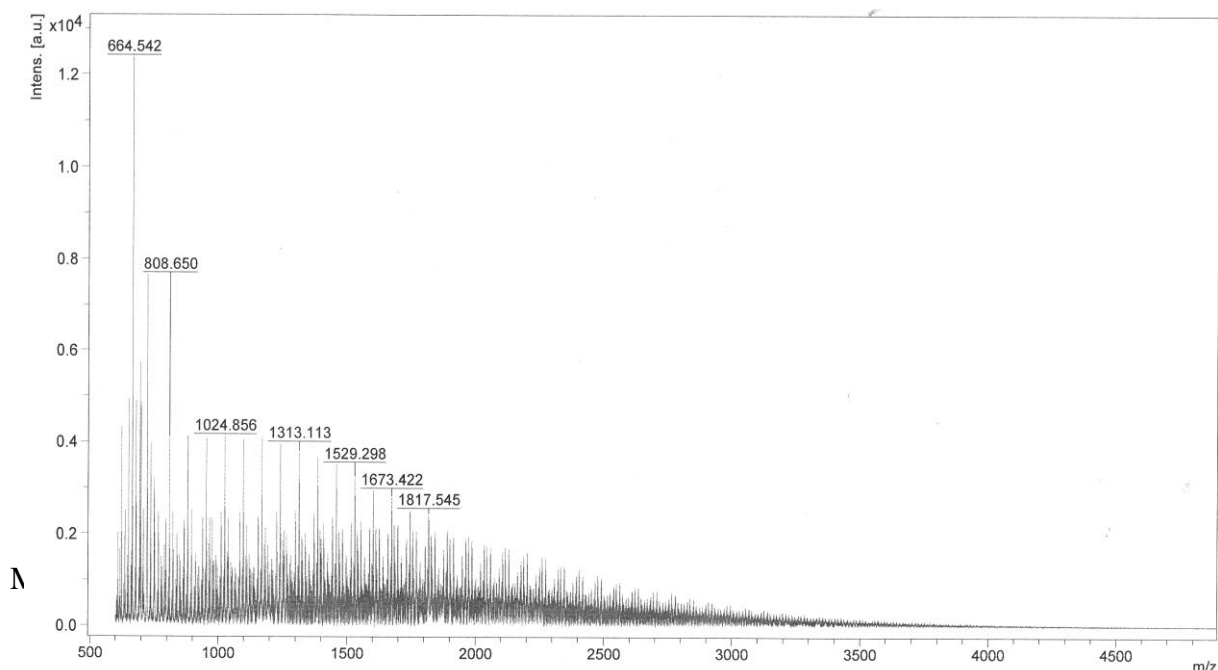
IR spectrum of p(THF-ECB)



GPC of p(THF-ECB)

### Synthesis of p(THF-EMO).

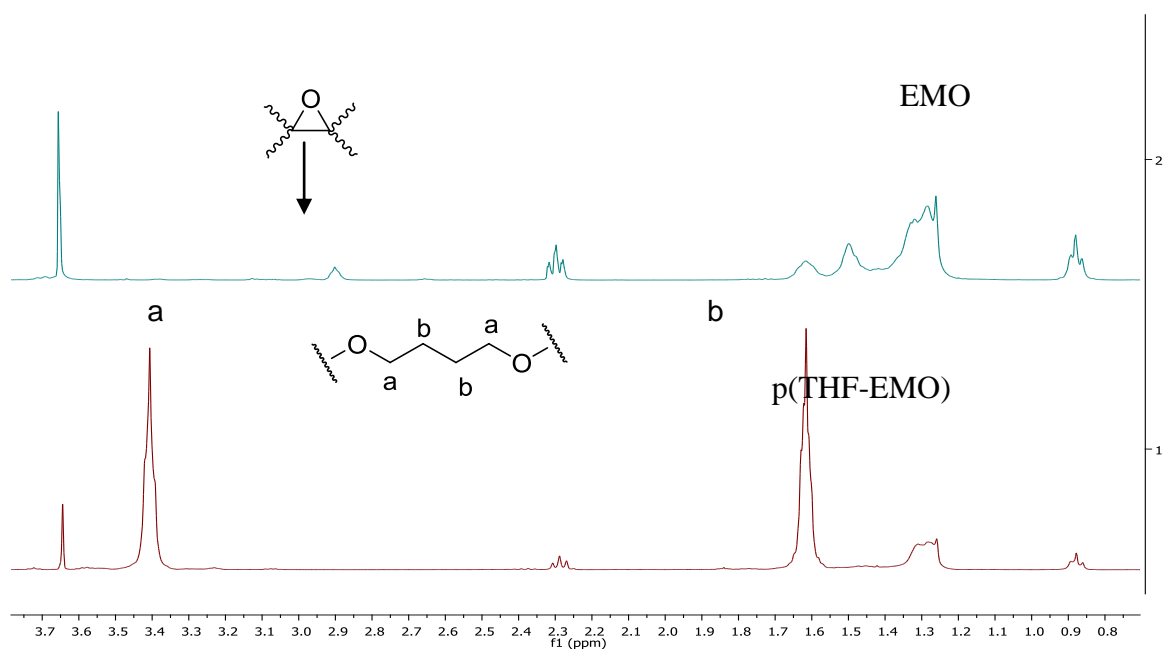
The experiment was conducted according to the procedure described above. Epoxidized methyl oleate (50 g, 160 mmol), dry tetrahydrofuran (1000 mL),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (1.13 g, 8 mmol), clear viscous liquid (78 g).  $\nu_{\text{max}}/\text{cm}^{-1}$  3353 (O-H) 2924, 2852 (C-H) 1739 (C=O) 1105 (C-O) 755 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 3.66 (3H, s,  $\text{CH}_3\text{O}$ ), 3.62-3.50 (2H, m,  $\text{CHO}$ ), 3.46-3.34 (92H, m,  $\text{CH}_2\text{O}$ ), 2.29 (2H, t,  $J$  = 7.5 Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.69-1.55 (94H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.50-1.20 (24H, m,  $\text{CH}_2\text{CH}_2$ ), 0.87 (3H, t,  $J$  = 7.0 Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 173.4 (C=O) 72.0, 70.1 ( $\text{HC-O}$ ) 50.7 ( $\text{H}_3\text{C-O}$ ), 33.4 ( $\text{O}=\text{CCH}_2$ ), 26.0 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 31.1, 29.2, 22.4 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.6 ( $\text{CH}_2\text{CH}_3$ ).



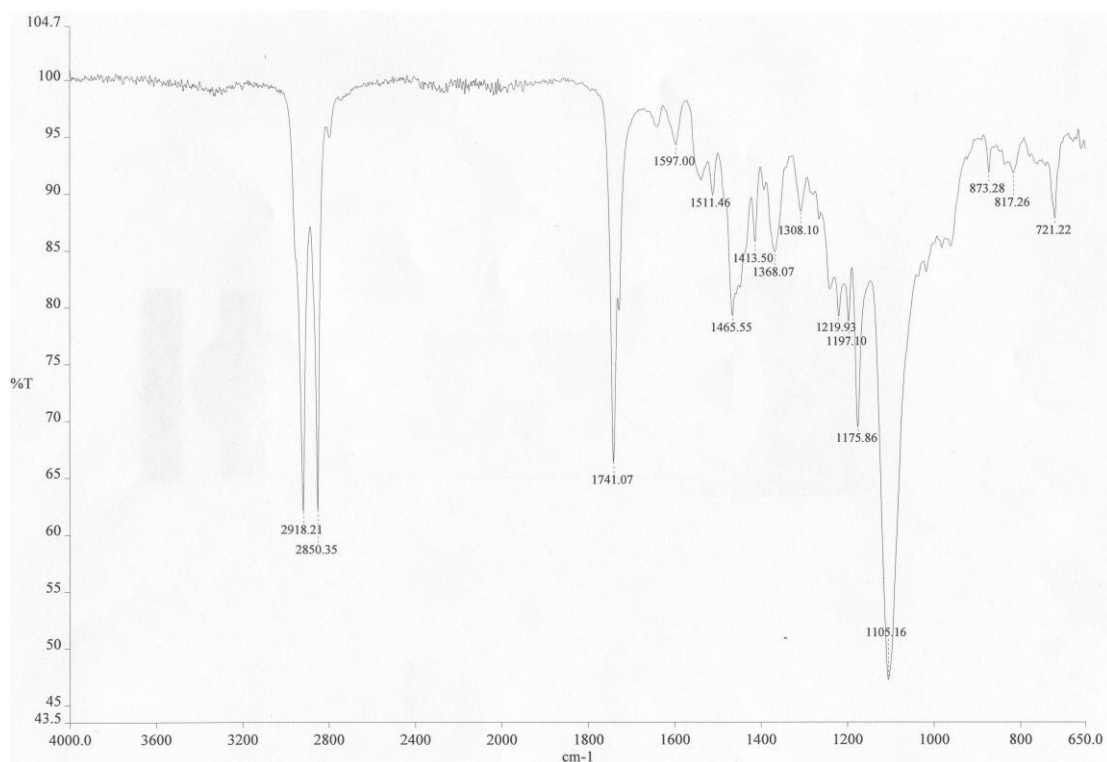
### Properties of p(THF-EMO)

Entry	Mol equivalent of BF <sub>3</sub> .Et <sub>2</sub> O	Yield (%)	Gel permeation chromatography		
			M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI
1	0.01	0	-	-	-
2	0.025	75	18K	8K	2.1
3	0.05	97	54K	26K	2.1

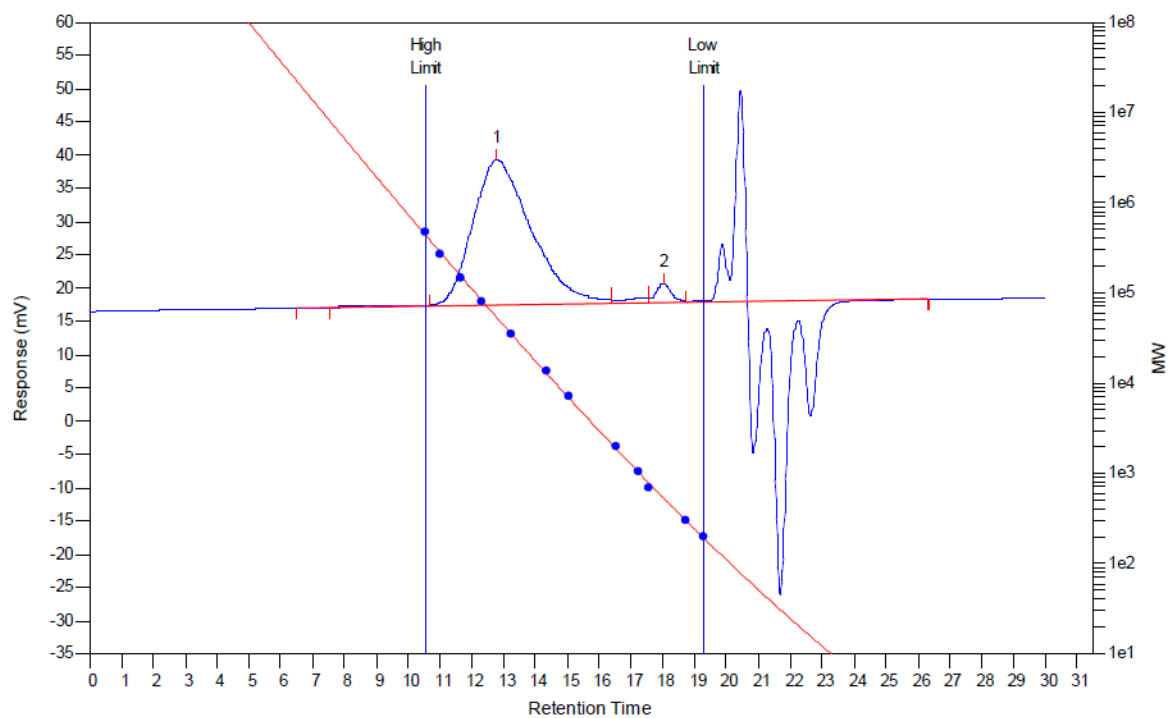
M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index



Stacked 400MHz <sup>1</sup>H NMR spectrum of EMO and p(THF-EMO) in CDCl<sub>3</sub>.



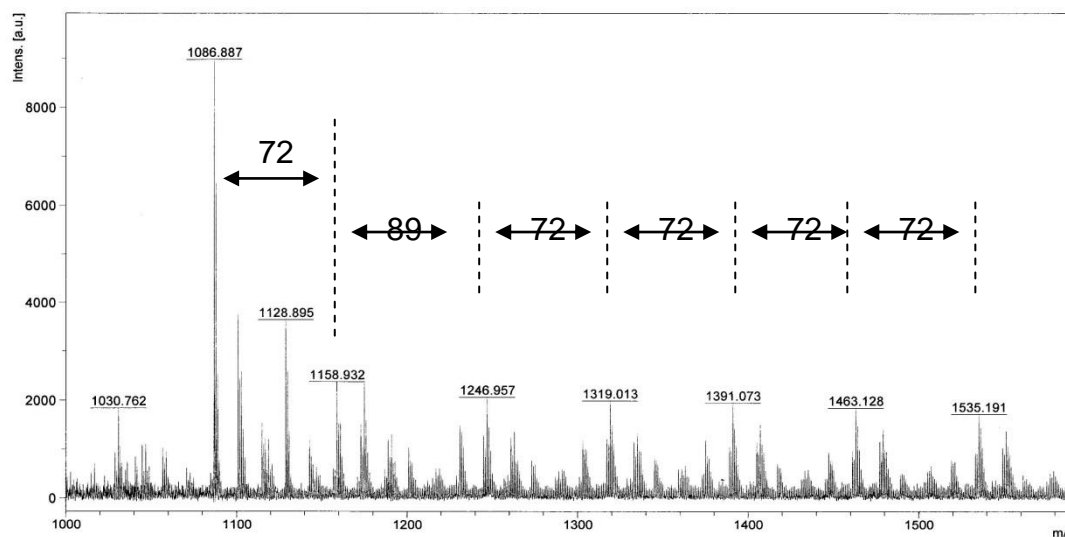
IR spectrum of p(THF-EMO)



GPC of p(THF-EMO)

### Synthesis of p(THF-EPO).

The experiment was conducted according to the procedure described above. Epoxidized palm oil (50 g, 56 mmol), tetrahydrofuran (2000 mL),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.32 g, 2.3 mmol), clear viscous liquid (403 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3355 (O-H) 2918, 2851 (C-H) 1742 (C=O) 1103 (C-O) 746 ( $\text{CH}_2$ )  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 5.27\text{-}5.20$  (1H, m,  $\text{CHO}$ ), 4.27 (2H, dd,  $J = 11.9$  Hz, 4.1 Hz,  $\text{CH}_2\text{O}$ ), 4.12 (2H, dd,  $J = 11.9$  Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.45-3.32 (400H, m,  $\text{HCO}$ ), 2.31 (6H, t,  $J = 7.8$  Hz,  $\text{O=CCH}_2\text{CH}_2$ ), 1.68-1.52 (406H, m,  $\text{O=CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.35-1.20 (64H, m,  $\text{CH}_2\text{CH}_2$ ), 0.86 (9H, t,  $J = 6.8$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 173.2$ , 172.8 (C=O) 70.6 ( $\text{HC-O}$ ) 68.9 ( $\text{HC-O}$ ), 62.2, 62.0 ( $\text{H}_2\text{C-O}$ ), 33.9 ( $\text{O=CCH}_2$ ), 26.3 ( $\text{O=CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 29.6, 22.5 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.9 ( $\text{CH}_2\text{CH}_3$ ).



MALDI-TOF-MS spectrum of p(THF-EPO) by using DHB as the matrix in the analysis

**The extent of copolymerisation of EPO with THF catalyzed by BF<sub>3</sub>.Et<sub>2</sub>O against time**

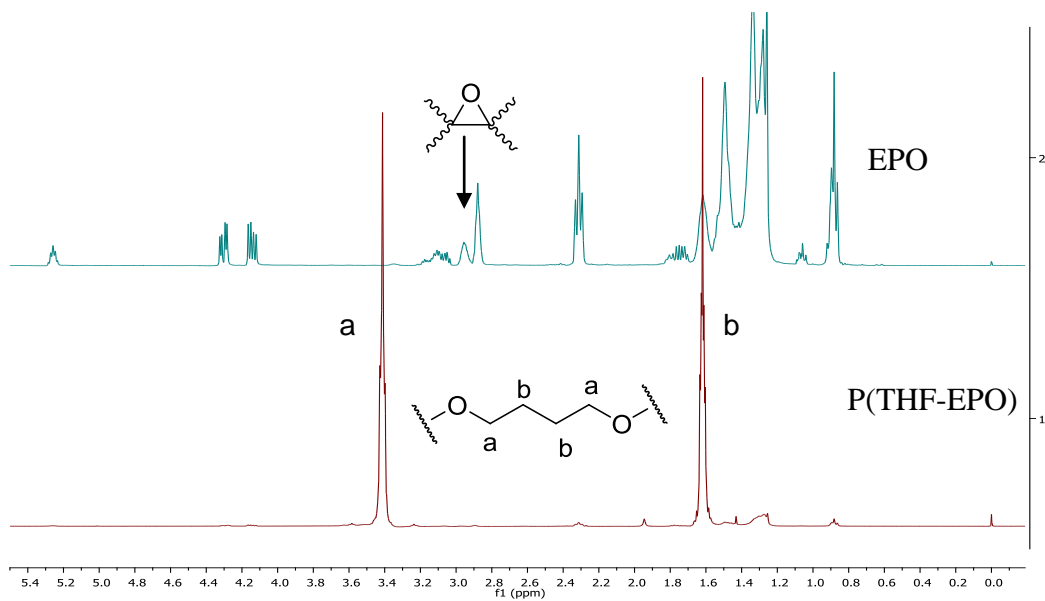
Reaction time (minutes)	Polymer content (%)	Gel permeation chromatography		
		M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI
5	2	28K	26K	1.1
30	22	51K	32K	1.6
60	37	64K	36K	1.8
120	54	88K	41K	2.2
240	65	112K	46k	2.4
480	73	150K	49K	3.1
720	78	181K	54K	3.4
1440	82	234K	59K	4.0

M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index

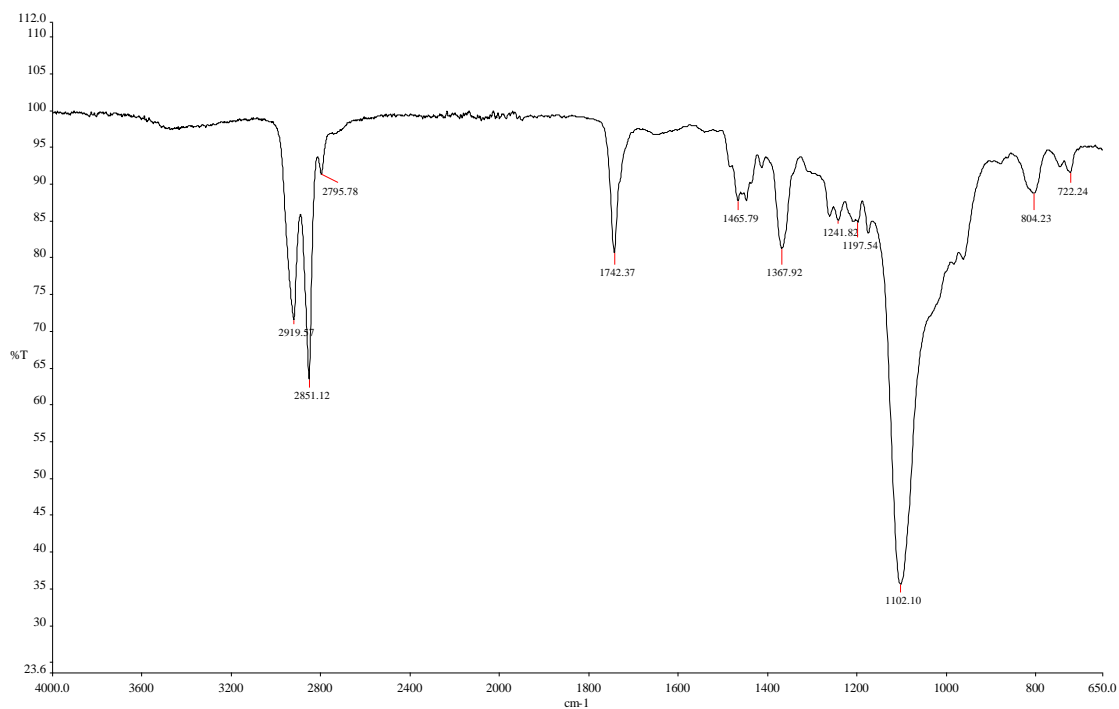
**Effect of monomer ratio THF : (EPO) on polymerization.**

Entry	Monomer ratio THF : (EPO) (ml : g)	Yield (%)	Gel permeation chromatography		
			M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI
1	4 : 1	Gelled	-	-	-
2	8 : 1	Gelled	-	-	-
3	12 : 1	Gelled	-	-	-
4	16 : 1	79	148K	45K	3.3
5	20 : 1	81	173K	56K	3.1
6	24 : 1	83	169K	56K	3.0

M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index

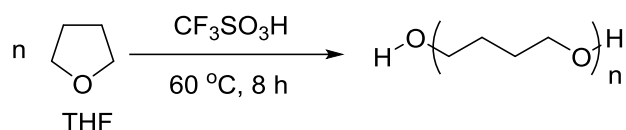


400 MHz  $^1\text{H}$  NMR spectrum of (EPO) and p(THF-EPO) in  $\text{CDCl}_3$



IR spectrum of p(THF-EPO)

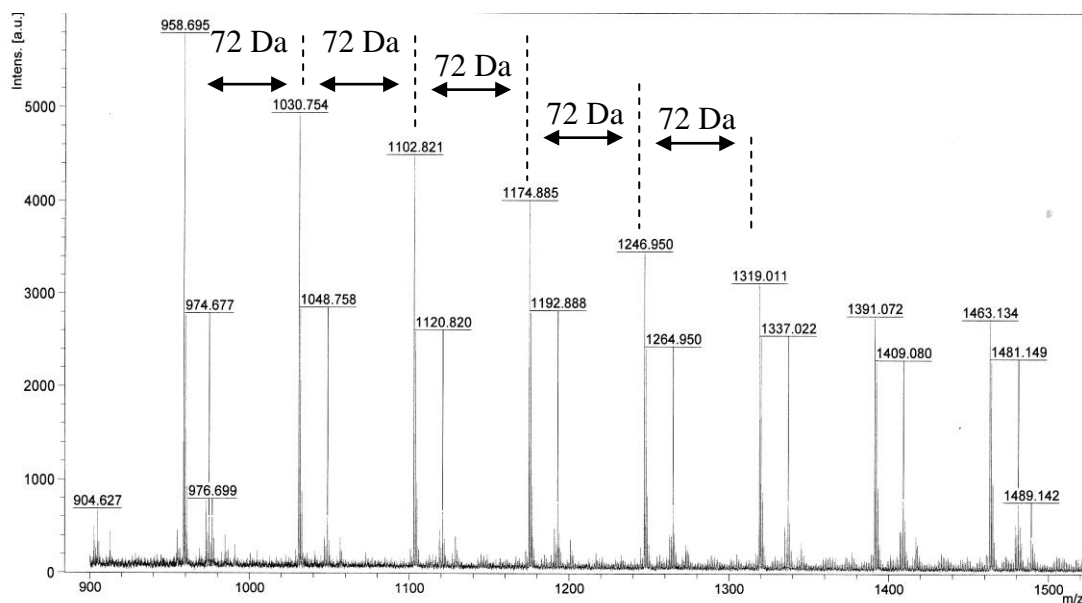
### Homopolymerisation of THF



The homopolymerization of THF was conducted according to method published by Dorai and Hida: S. Dorai and G. A. Hida, *US Patent* 1992, 5155283.

Mol eq.	Polymer content (%)	GPC			OHV	AV
		$M_w$ (Da)	$M_n$ (Da)	PDI		
0.08	100	33800	18000	1.87	40	0.5

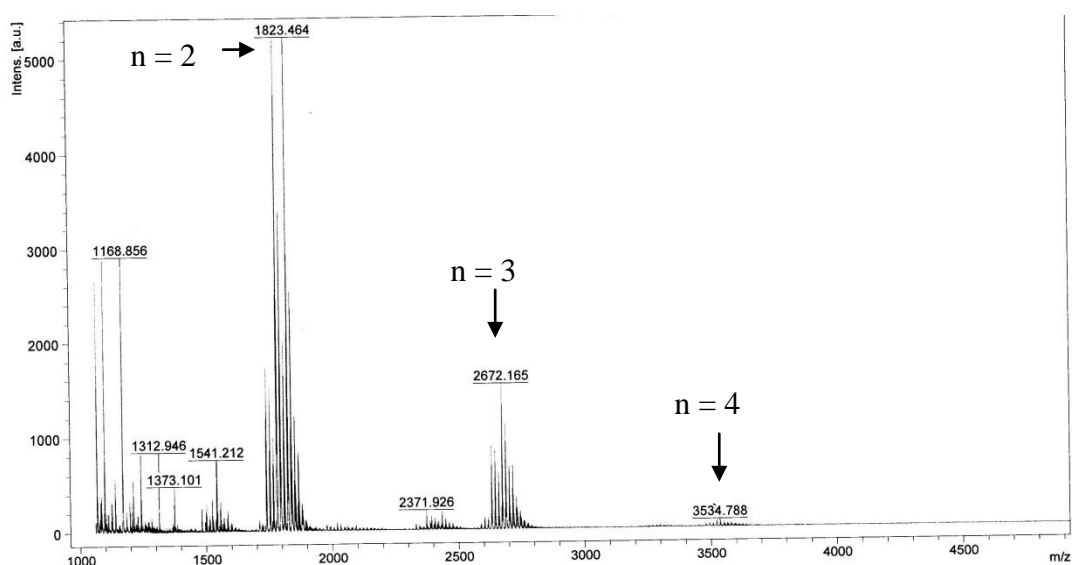
Mol eq. = mol equivalent of  $\text{CF}_3\text{SO}_3\text{H}$ , GPC = gel permeation chromatography,  $M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index, OHV = hydroxyl value (mg KOH/g), AV = acid value (mg KOH/g)



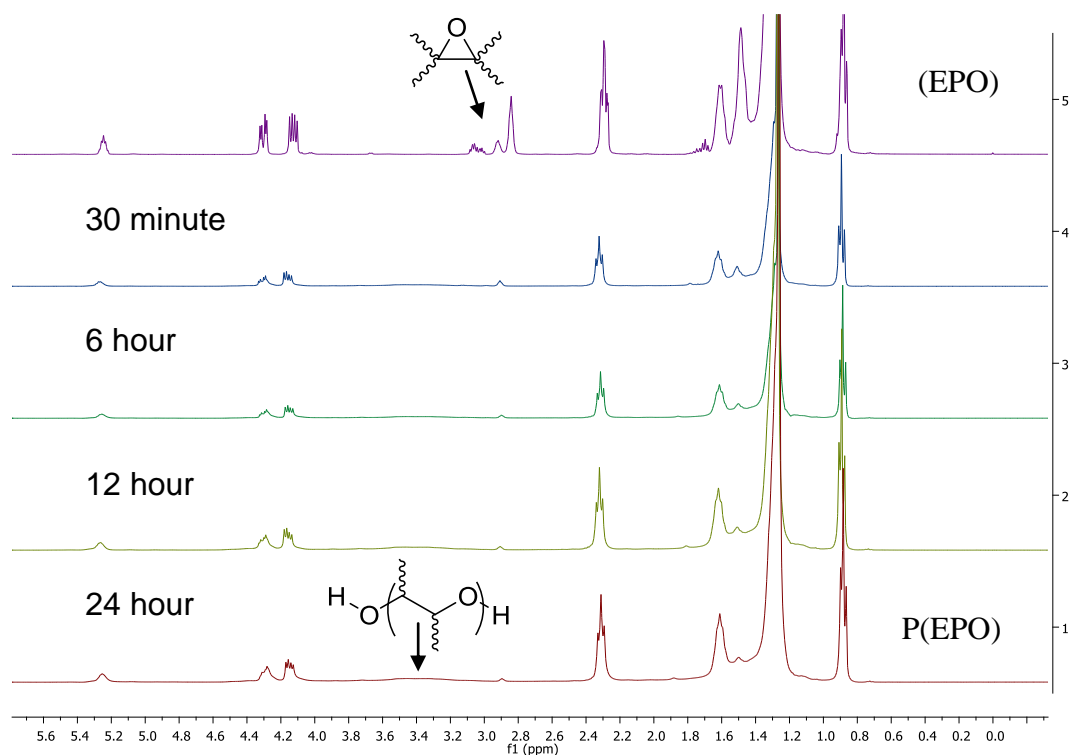


## Homopolymerisation of epoxidized palm oil (EPO).

To epoxidized palm oil (EPO) (100 g, 112 mmol) in hexane (600 mL) at 20 °C under N<sub>2</sub> was added BF<sub>3</sub>.Et<sub>2</sub>O (1.1g, 7.8 mmol) drop-wise. After the addition of BF<sub>3</sub>.Et<sub>2</sub>O was completed, the reaction temperature was maintained at 20 °C for another 24 hours. Then, the reaction mixture washed with saturated NaHCO<sub>3</sub> solution (250 mL). The aqueous layer was separated from the organic layer and CHCl<sub>3</sub> (500 mL) was added. The organic layer was washed with NaCl solution (200 mL), dried over MgSO<sub>4</sub> and the solvent removed *in vacuo* to provide a yellowish liquid (98.4 g);  $\nu_{\max}/\text{cm}^{-1}$  3348 (O-H) 2921, 2851 (C-H) 1742 (C=O) 1459 (CH<sub>2</sub>) 1158 (C-O) 722 (CH<sub>2</sub>) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.22-5.13 (1H, m, CHO), 4.21 (2H, dd,  $J$  = 11.9 Hz, 4.1 Hz, CH<sub>2</sub>O), 4.07 (2H, dd,  $J$  = 11.8 Hz, 5.9 Hz, CH<sub>2</sub>O), 3.80-3.00 (4H, m, HCO), 2.23 (6H, t,  $J$  = 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.60-1.47 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.35-1.10 (64H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.79 (9H, t,  $J$  = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 173.2, 172.5 (C=O) 72.4 (HC-O) 68.8 (HC-O), 61.8, 61.6 (H<sub>2</sub>C-O), 33.9 (O=CCH<sub>2</sub>), 24.7 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.5, 22.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>).



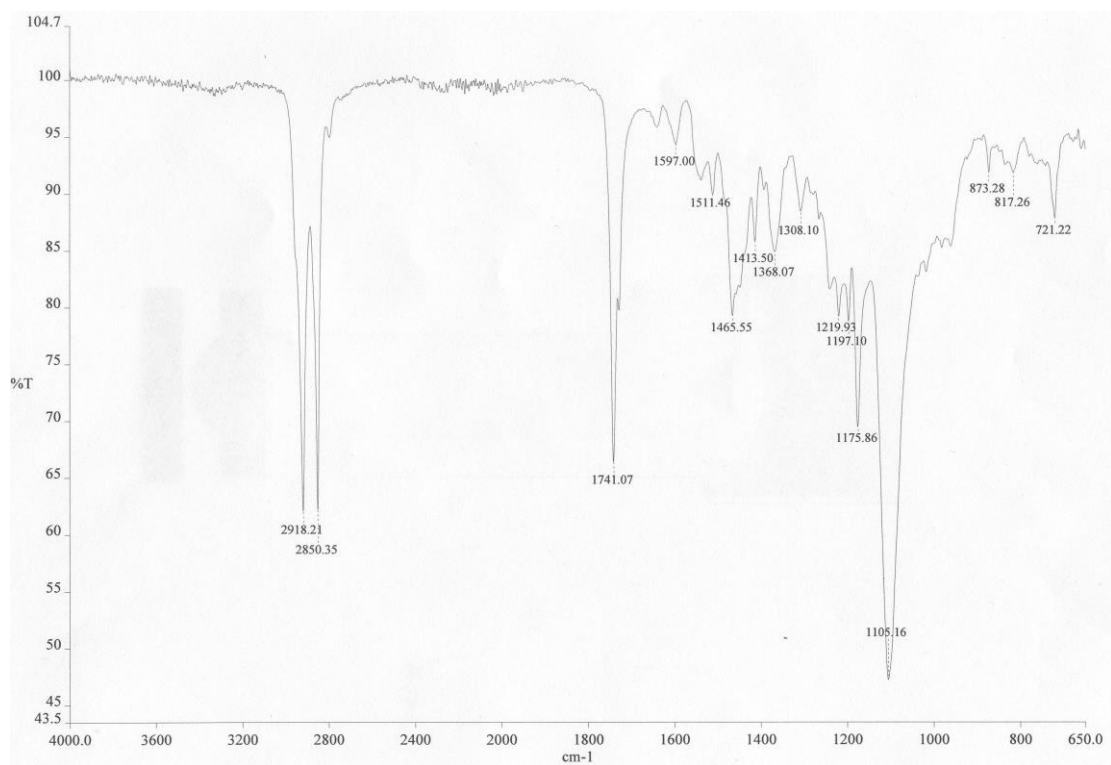
MALDI-TOF-MS spectrum of p(EPO) by using DHB as the matrix in the analysis



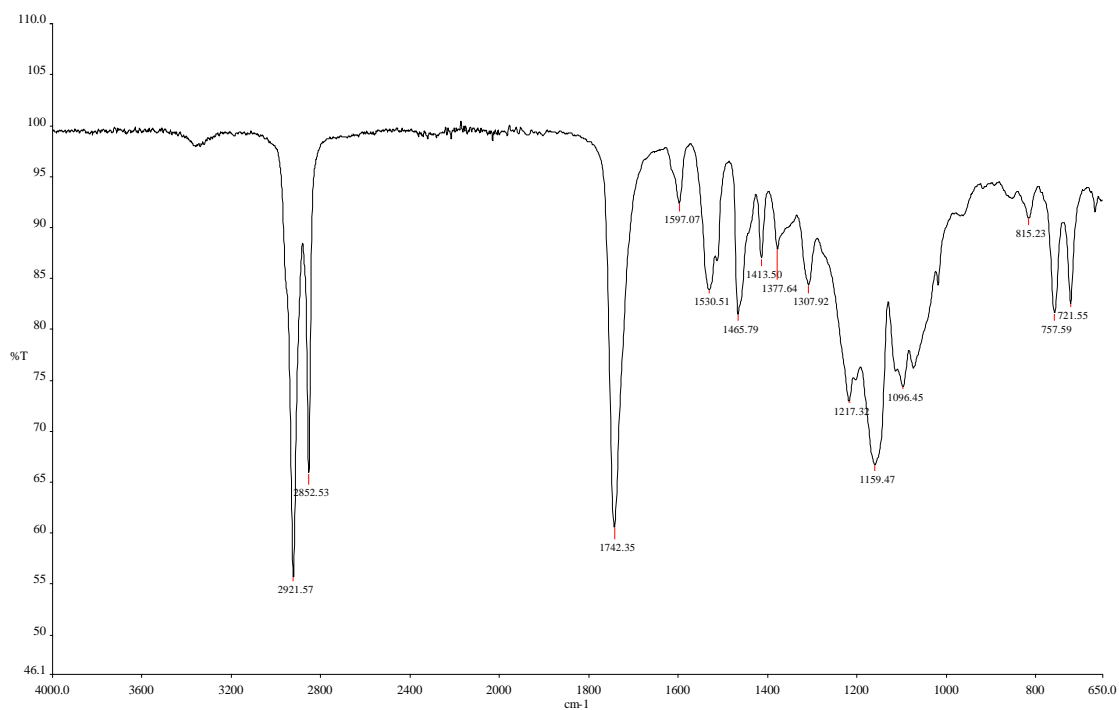
400 MHz <sup>1</sup>H NMR of polymerization of EPO at certain reaction time in CDCl<sub>3</sub>

**General Procedure for Polyurethane made from p(THF-EVO) and MDI: Example synthesis of p(THF-EPO-MDI).**

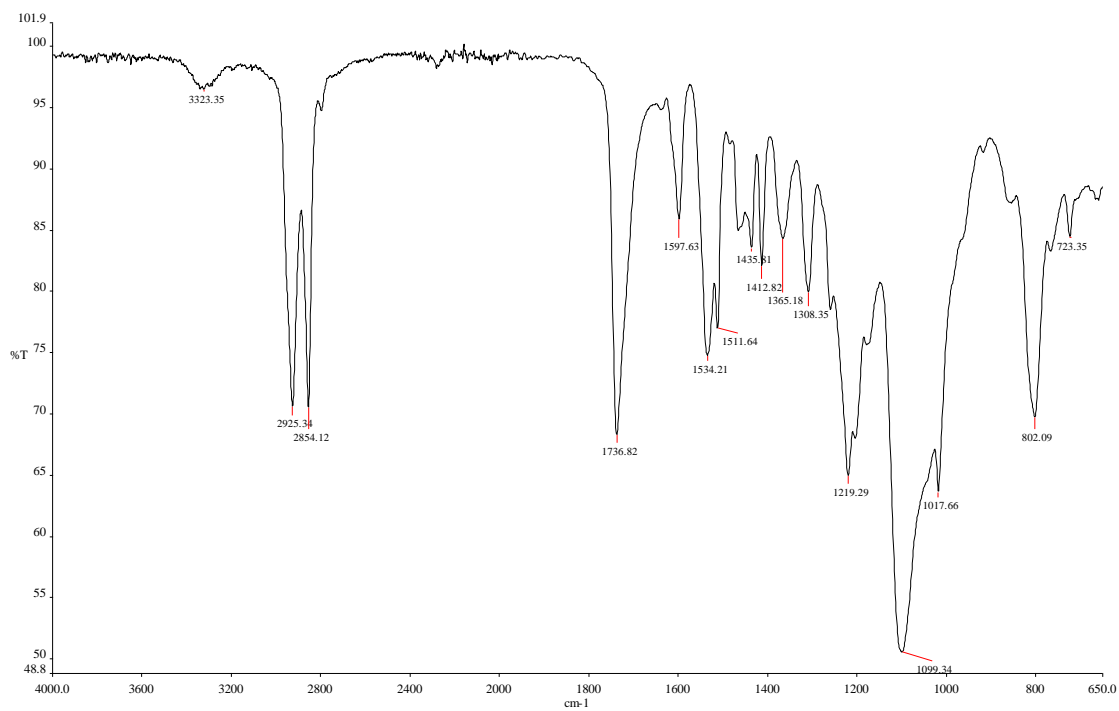
P(THF-EPO), (10 g, hydroxyl value = 30.5 mg KOH/g sample) was dissolved in dry chloroform (150 mL) under N<sub>2</sub>. 4,4'-Methylene diphenyldiisocyanate (MDI) (1.7 g) was added. (The NCO/OH ratio index was 1.02). The reaction mixture was heated to 60 °C and the crude polyurethane was poured into a pre-heated mold at 60 °C. The polyurethane was cured at 60 °C for 24 hours.



IR spectrum of p(THF-EMO-MDI)



IR spectrum of p(THF-ECB-MDI)



IR spectrum of p(THF-EPO-MDI)