Supporting Information

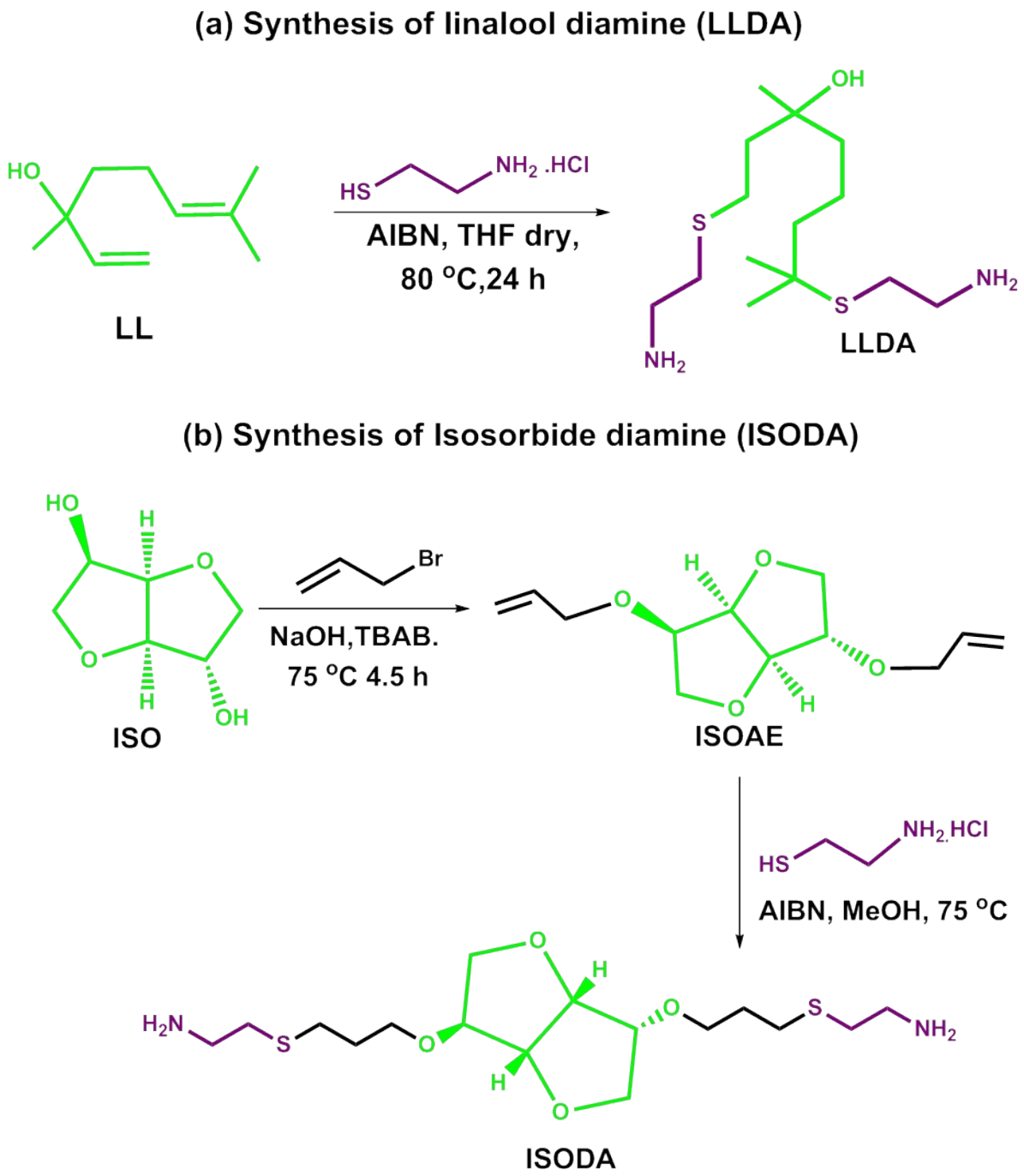
Biodegradable isocyanate free polyurethanes films via noncatalytic route: facile modified polycaprolactone triol and biobased diamine as precursors

Dinesh Kumar Chelike and Senthil A. Gurusamy Thangavelu*

Department of Chemistry, SRM Institute of Science and Technology, Kattankulathur Chennai 603 203

Tamil Nadu, India Email: senthilt1@srmist.edu.in, senthilagt@gmail.com

Contents **Page No.**



Scheme S1. Synthesis of sustainable diamine precursors, a) linalool diamine (LLDA) and b) isosorbide diamine (ISODA) [3].

Experimental section

Materials

Polycaprolactone triol (PCL, CAPA 3201, ~ M.W. 2000, waxy solid at RT, M.P.: 40-50 °C, OH value: 85.85) was received as the gift sample from Perstrop India Ltd. and glycerol 1,2-carbonate from IndiaMART Mumbai, India. Isosorbide, (∓)-3,7-dimethyl-3-hydroxy-1,6-octadiene (linalool), 2-mercaptoethylamine hydrochloride were procured from Sigma Aldrich and phosphate buffer saline (PBS) solution (pH=7.2) salt was procured form Loba Chemical PVT. Ltd., India. Triethylamine, methanol, chloroform, dichloromethane, hexane, toluene, acetone, dioxane, sodium hydroxide (NaOH), tetrahydrofuran (THF), N,N'-dimethylformamide (DMF), tetra-n-butylammonium bromide (TBAB), succinic anhydride, dimethylaminopyridine (DMAP), N,N-dicyclohexylcarbodiimide (DCC), allyl bromide and azobisisobutyronitrile (AIBN) were procured from Siscon Research Laboratories PVT. Ltd., India.

Methods

FT-IR spectra for all these samples were collected using IRTracer-100 Shimadzu by ATR FT-IR mode. Raman spectra was recorded from Micro-Raman Spectrometer HORIBA France, LABRAM HR Evolution under 633 nm wavelength. ^{1}H and ^{13}C NMR spectra of the samples were acquired in Bruker 500 MHz Bruker Avance III NMR instrument, with respect to ^{13}C probe with frequency at 100 MHz using 4 mm probe head. Top Spin NMR software was accessed to process the acquisition data into NMR spectra. HR-MS data for the samples was performed from LC/MS 6230B by the system of time-of-flight (TOF). MALDI-TOF-MS was executed to obtain mass from Agilent technology, Ultra fleXtreme Bruker. Thermogravimetric analysis (TGA) was implemented for each sample upon heating @ 10 °C min^{-1} from STA 2500 REGULUS-TGA-DSC Thermal analyser over the range of ambient temperature to 600 °C under nitrogen flow and differential scanning calorimetry (DSC) was recorded around ambient

condition to 300 ℃ to determine the glass transition temperature (T_g). Water contact angle was measured at ambient condition by using 2 μL of Milli-Q water through sessile drop method from DMs-401, Japan. The solid state ^{13}C NMR data was collected from Bruker Avance III HD 400 WB NMR spectrometer at resonance frequency of 100.61 MHz for ^{13}C nuclei.

Synthesis of succinic acid derivative of polycaprolactone triol [PCL-$(COOH)_3$]

PCL-$(COOH)_3$ was prepared by the modified synthetic protocol from the previous report [1]. PCL (8.5 g, 4.25 mmol) was taken in RB flask (100 mL) and melted at 60 °C prior to the addition of dioxane (15 mL) and stirred for 30 min. The freshly distilled Et_3N (2.47 mL, 12.83 mmol) was added to the above solution and stirred at ambient temperature for 3 h. Succinic anhydride (1.2 g, 12.83 mmol) in dioxane (15 mL) was added into the above reaction mixture followed by addition of DMAP in a form of solid (1.57 g, 12.83 mmol), stirred for 24 h at ambient temperature. The reaction mixture was filtered and concentrated under vacuum to obtain the white waxy solid, further purified by methanol to isolate the colourless semisolid product. Yield: 12.30 g, 79 %, ^1H NMR ($CDCl_3$, 500 MHz) 0.84 (t, 3H, **g**), 1.34 (**e**), 1.60 (m, **d,f**), 2.26 (m, **c**), 2.58 (s, **j**), 3.13 (s, **i**), 3.59 (t, **b**), 3.97-4.03 (m, **a, h**) and 6.04 (COOH group), ^{13}C NMR (125 MHz, ppm) 7.34 (1), 24.56 (7), 25.52 (8), 28.24 (9), 28.33 (2), 33.98 (6 and 12), 40.66 (3), 62.57 (4), 63.62 (10), 64.17 (13), 172.24 (11 and 14) and 173.81 (5), FT-IR (cm^{-1}) 3496 (m, -O-H str.), 2951 (m, -C-H str.), 1730 (s, C=O), 1254 (m, -C-C), 1162 (s, -C-O-C), MALDI-mass: 2314 [M^+] ion peak.

Synthesis of polycaprolactone glycerol carbonate derivative [PCL-$(COOGC)_3$]

PCL-$(COOGC)_3$ was prepared by the modified synthetic protocol from the previous report [1]. PCL-$(COOH)_3$ (5 g, 2.18 mmol) and DCC (1.35 g, 6.56 mmol) were charged in RB flask (100 mL) and dissolved in dry DCM (20 mL) by stirring at ambient temperature for 1 h. DMAP (0.802 g, 6.56 mmol) and glycerol 1,2-carbonate (0.775 g, 6.56 mmol) were added into the addition funnel charged with dry DCM (15 mL) and added drop wise for 15 minutes into

the above reaction mixture and stirred for 24 h at ambient temperature. The above reaction mixture was filtered and filtrate was evaporated under vacuum to obtain colourless semisolid product, washed with 2 N HCl to eliminate the excess DMAP to isolate colourless viscous solid. Yield: 5.39 g, 97 %, ^{1}H NMR ($CDCl_3$, 500 MHz) 0.87 (t, 3H, **f**), 1.30-1.40 (m, **e**), 1.65 (m, **d**), 2.30-2.33 (t, **c**), 2.63-2.64 (s, **g, h**), 3.64-3.70 (m, **b**), 4.02-4.08 (m, **a, i**), 4.50-4.52 (d, 6 H, **k**), 4.80 (m, 3H, **j**),^{13}C NMR (125 MHz, ppm) 7.34 (1), 24.46 (7), 24.64 (8), 28.30 (9), 28.86 (2), 34.07 (6), 34.87 (12), 40.63 (3), 51.78 (4), 53.45 (16), 55.69 (15), 62.43 (17), 63.56 (10), 63.92 (13),156.94 (18) and 172.07-173.71 (5, 11 and 14), FT IR (cm^{-1}) : 2943 (m, -C-H str.), 1798 (m, GC, C=O), 1730 (s, ester, C=O), 1231 (s, -C-C), 1157 (m, -C-O-C), MALDI-mass: 2436 [M^{+}] ion peak.

Synthesis of isosorbide diallyl ether (ISOAE)

ISOAE was synthesised by a modified synthetic protocol from the previous report [2]. Isosorbide (3g, 20.5 mmol) and TBAB (0.300 g, 9.3 mmol) were taken in high pressure tube (100 mL) capped with rubber septa and dissolved in aq. NaOH (2 N, 12 mL). To the above reaction mixture, allyl bromide (10 mL, 1.2 mmol) was added drop wise and stirred for 1 h at ambient condition under N_2 atmosphere. After closed the tube by teflon cap, the reaction mixture was heated in oil bath for 4 h at 75 ˚C. The reaction mixture was cooled down to attain room temperature and washed with diluted HCl solution (2 N, 10 mL) followed by deionized water (3×10 mL) prior to extraction by DCM (3×40 mL). The extract was dried with anhydrous Na_2SO_4 and filtered before evacuated the solvent under reduced pressure to obtain the yellow colour liquid compound. Yield: 2.50 g, 54 %, ^{1}H NMR ($CDCl_3$, 500 MHz) 3.48-3.51 (t, 1H, **h**), 3.81-3.3.97 (m, 8H, **g, g', h', i** and **i'**), 4.09-4.12 (d, 1H, **d, d', e** and **e'**), 4.41-4.53 (dd, 2H, **f, f'**), 5.07-5.22 (m, 4H, **c ,c', b** and **b'**), 5.81 (m, 2H, **a** and **a'**), ^{13}C NMR (125 MHz, ppm) 69.34 (5'), 69.96 (5), 71.08 (3'), 72.93 (3), 78.99 (4'), 79.74 (4), 83.27 (6'), 85.78 (6),

117.17 (1,1'), 134.10 (2,2'), FT-IR (cm^{-1}) 2959 (m, C-H str.), 1669 (m, C=C str.), 1469 (m, C-H ben.), 1078 (s, C-O-C), 928 (m, C=C ben.), HRMS 227.1278 [M^+] ion peak.

Synthesis of isosorbide diamine (ISODA)

ISODA was prepared by the modified synthetic protocol from the previous report [3]. ISOAE (0.616 g, 2.73 mmol) was taken in RB flask (50 mL) and dissolved in MeOH (20 mL) prior to addition of 2-mercaptoethylamine hydrochloride (0.773 g, 6.8 mmol), stirred for 1 h at ambient condition. To the above reaction mixture, AIBN (0.223 g, 1.36 mmol) was into six fractions and added over the range of 1h into above medium prior to the reaction mixture was heated to reflux at 80 ˚C for 26 h. After the reaction mixture was cooled down to ambient temperature, NaOH pellets (~ 0.8 g) added slowly under stirring at ice cold condition to raise the pH value of the reaction medium up to 10. The reaction mixture was filtered and the filtrate was evaporated under vacuum to obtain viscous product, which was extracted by DCM (3×30 mL) to obtain the yellow viscous compound. Yield: 0.937 g , 90 %, ^{1}H NMR ($CDCl_3$, 500 MHz) 1.80-1.90 (t, 4H, **Hd, Hd'**), 2.65-2.85 (m, 3H, **Hc, Hc'**), 2.86-2.97 (m, 4H, **Hb, Hb'**), 3.12-3.31 (m, 4H, **Ha, Ha'**), 3.53-3.60 (m, 4H, **He, He'**), 3.73-4.06 (m, 8H, **Hg, Hg',Hh** and **Hh'**), 4.49-4.52 (m, 1H, **Hf'**), 4.64 (m, 4H, **Hf**), ^{13}C NMR (125 MHz, ppm) 28.26 (3,3'), 29.68 (4,4'), 30.78 (2,2'), 39.69 (1,1'), 67.32 (5'), 69.03 (5), 70.58 (7'), 71.72 (7), 79.51 (6'), 80.49 (6), 83.72 (8'), 84.49 (8), FT-IR (cm^{-1}) 3266 (m, N-H str.), 2926 (m, C-H), 1615 (m, -N-H ben.), 1453 (m, -C-H ben), 1554 (m, -C-N), 1093 (s, C-O), HR-MS: 381.1874 [M^+] ion peak.

Synthesis of linalool diamine (LLDA)

LLDA was obtained by the modified synthetic protocol from the previous report [4]. Linalool (1.6 g, 10.38 mmol) was weighed in RB flask (50 mL) and dissolved in dry THF (20 mL) prior to the addition of 2-mercaptoethylamine hydrochloride (4.72 g, 41.49 mmol), stirred for 1 h at ambient temperature. AIBN (0.137 g, 0.830 mmol) was added portion wise then reaction mixture was allowed to stir for overnight. Further, reaction mixture was allowed to

reflux at 80 ˚C for 24 h, after completion of reaction NaOH (pellets) added into the same to maintain pH=10 and washed with distilled water before the extraction using chloroform (3× 35 mL). The organic layer was dried by anhydrous Na_2SO_4 and filtered before evaporation under high vacuum to obtain the viscous yellow compound. Yield: 1.6 g , 50 % , ^{1}H NMR ($CDCl_3$, 500 MHz) 0.86 (d, 3H, **c**), 0.90 (d, 3H, **d**), 1.01 (d, 3H, **h**), 1.26-1.36 (m, 2H, **e**), 1.47-1.58 (m, 4H, **g** and **f**), 1.76-1.85 (m, 2H, **i**), 2.32-2.37 (m, 2H, **j**), 2.41-2.47 (m, 4H, **b** and **b'**), 2.58-2.64 (m, 4H, **a** and **a'**), ^{13}C NMR (125 MHz, ppm) 19.12 (6), 19.51 (11), 22.47 (9), 26.05 (2), 26.98 (4 and 4'), 31.89 (12), 34.76 (13), 35.15 (1), 41.00 (7), 41.80 (5), 42.13 (10), 53.97 (3) and 71.13 (8), FT-IR (cm^{-1}) 3344 (-NH and -OH str.), 2953 (-C-H str.), 1648 (-N-H ben.), 1586 (-C-N), 1460 (-C-H ben.), 1376 (-OH ben), 1102 (-C-O), HRMS 309.2028 [M+1$^+$] ion peak.

Synthetic formulation of isocyante free PU

PU formulations were performed by the modified procedure reported earlier [5]. PCL-$(COOGC)_3$ (4 g, 1.657 mmol) and diamine (HMDA, 0.193 g, 1.657 mmol) were taken in equal stoichiometric ratio (1:1) into the scintillation vial (15 mL) and dry DMF (1.5 mL) was added into the same to reduce the viscosity of medium. The reaction mixture was stirred at 110 ˚C for 8 h. After completed the reaction, homogenous transparent reaction mixture was transferred into the Petri dish to cure the sample at 90 ˚C to recover the dark, shiny and flexible film.

The above protocol was followed for the formulation of other two PU films by variation of the appropriate diamine (ISODA and LLDA) and reaction condition as shown in **Table S1**.

Table S1. Reaction composition of PU-1, PU-2 and PU-3 films

Sample	Cyclic carbonate	Diamine	Duration
PU-1	PCL-$(COOGC)_3$ (4 g, 1.657mmol)	HMDA (0.193 g, 1.657 mmol)	8 h
PU-2	PCL-$(COOGC)_3$ (4 g, 1.657mmol)	ISODA (0.630 g, 1.657 mmol)	15 h
PU-3	PCL-$(COOGC)_3$ (4 g, 1.657mmol)	LLDA (0.510 g, 1.657 mmol)	5 h

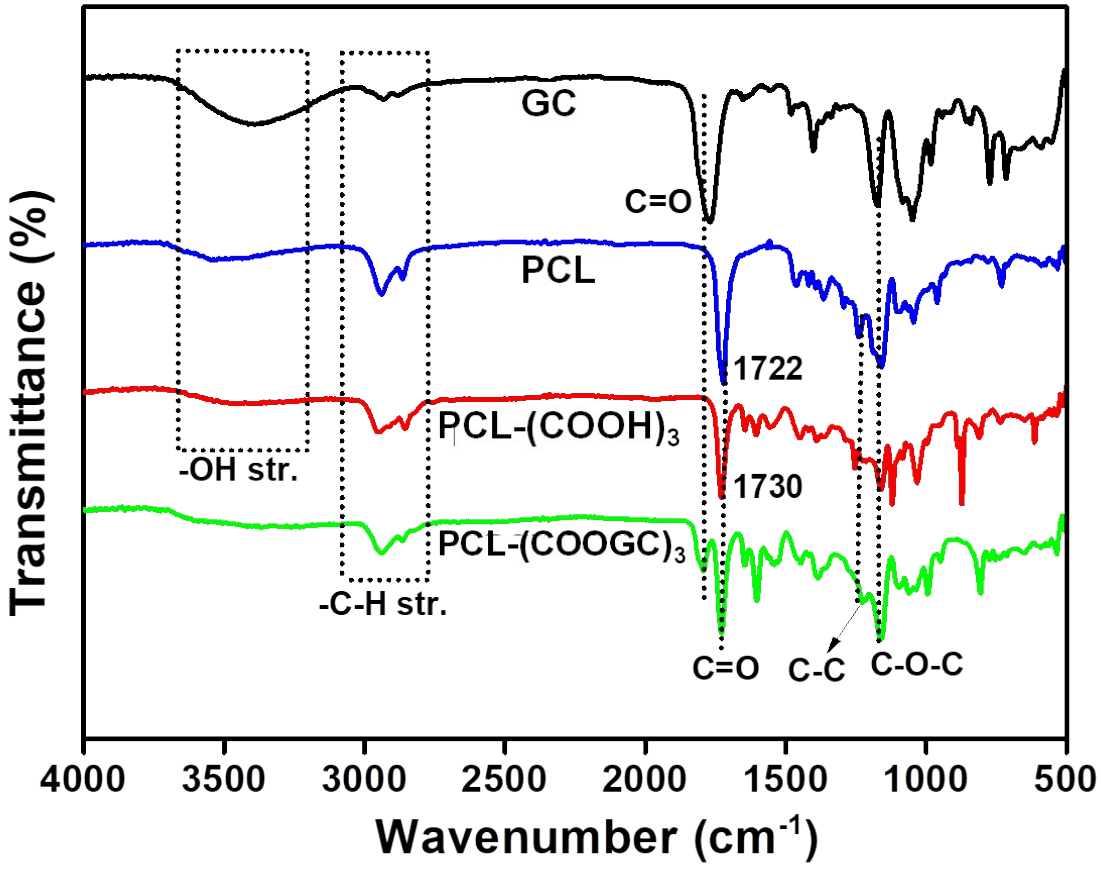


Figure S1. FT-IR spectra of GC, PCL, PCL-$(COOH)_3$ and PCL-$(COOGC)_3$.

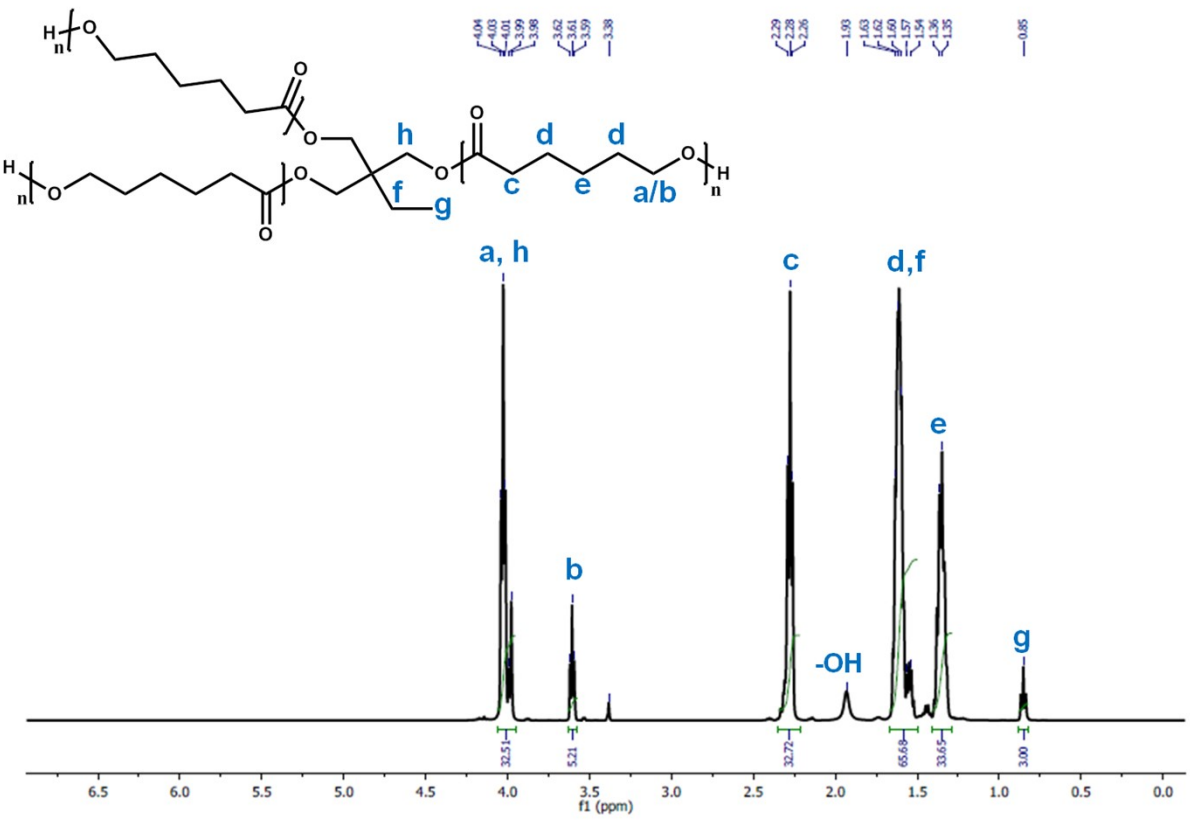


Figure S2. ^{1}H NMR of polyol, polycaprolactone triol (PCL).

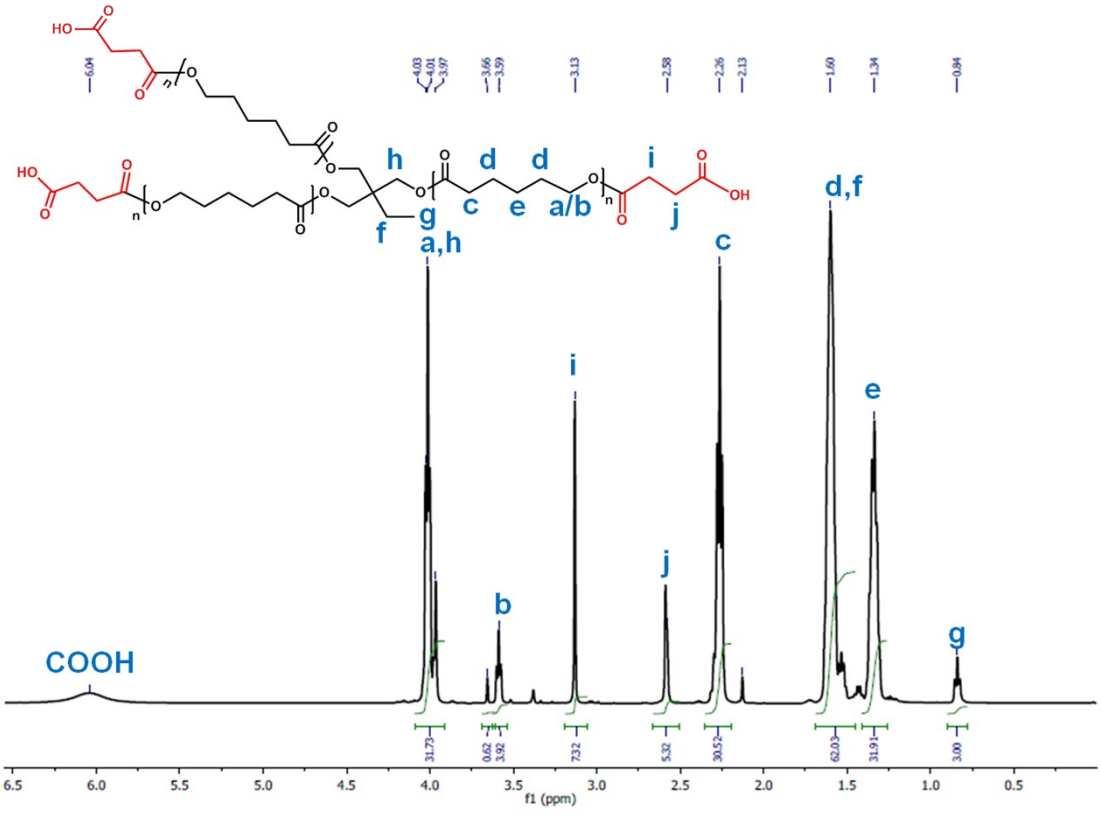


Figure S3. ^{1}H NMR of succinic acid derivative of PCL, PCL-$(COOH)_3$.

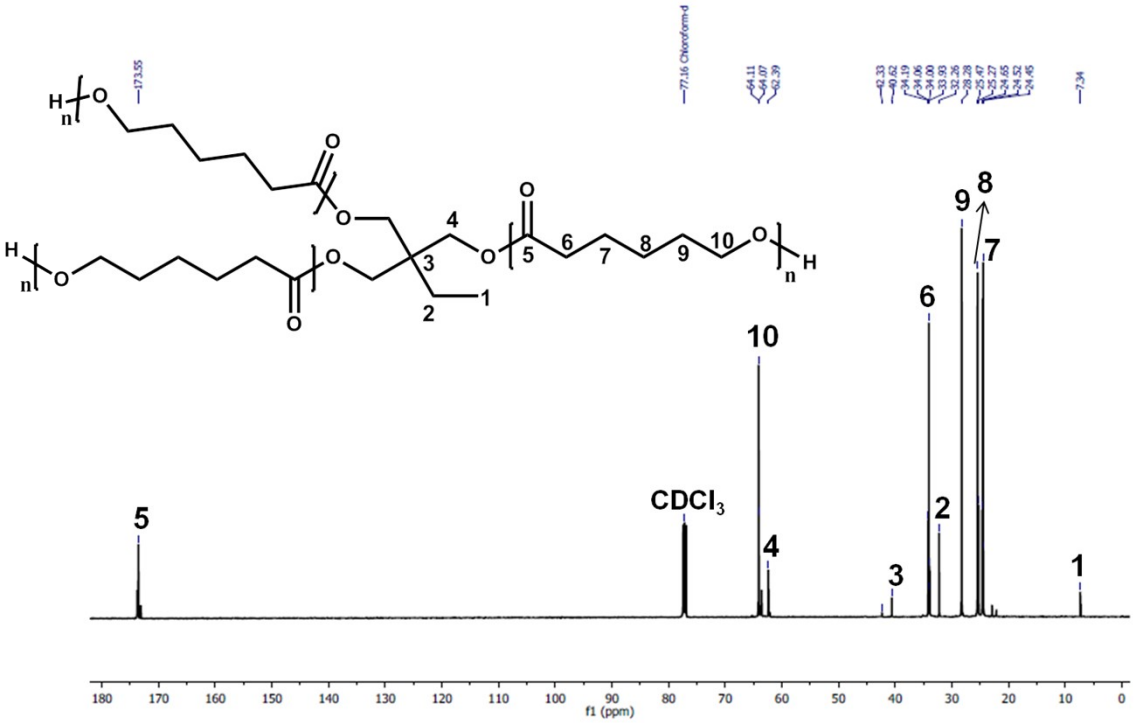


Figure S4. ^{13}C NMR of polyol, polycaprolactone triol (PCL).

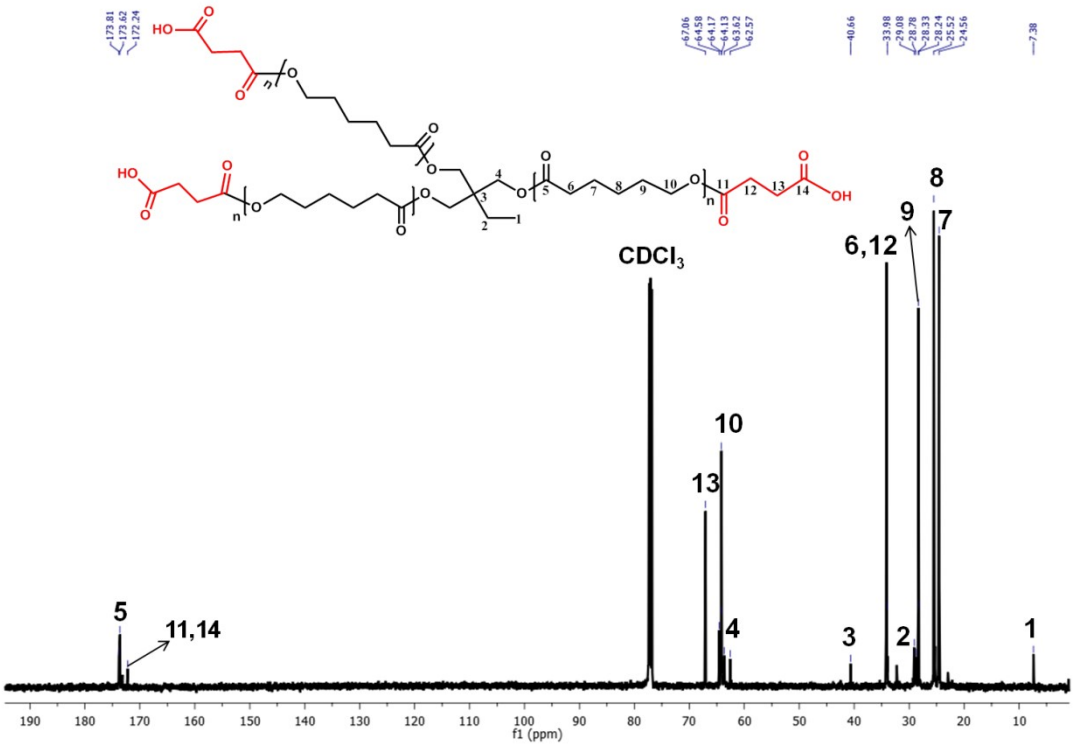


Figure S5. ^{13}C NMR of succinic acid derivative of PCL, PCL-$(COOH)_3$.

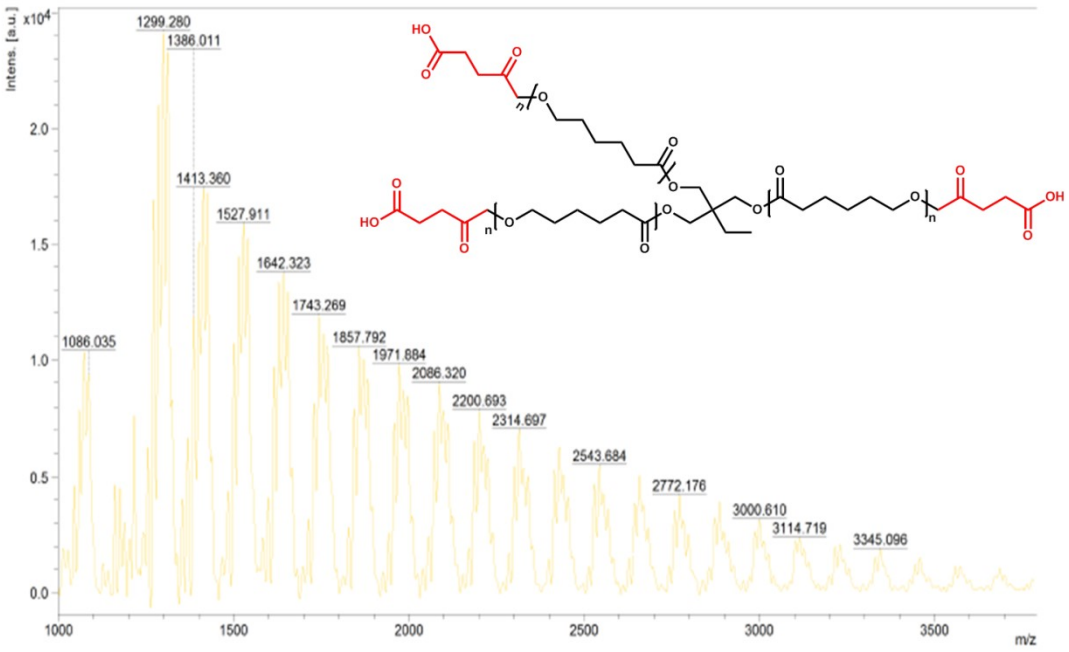


Figure S6. MALDI-TOF mass data for succinic acid derivative of PCL, PCL(COOH)$_3$.

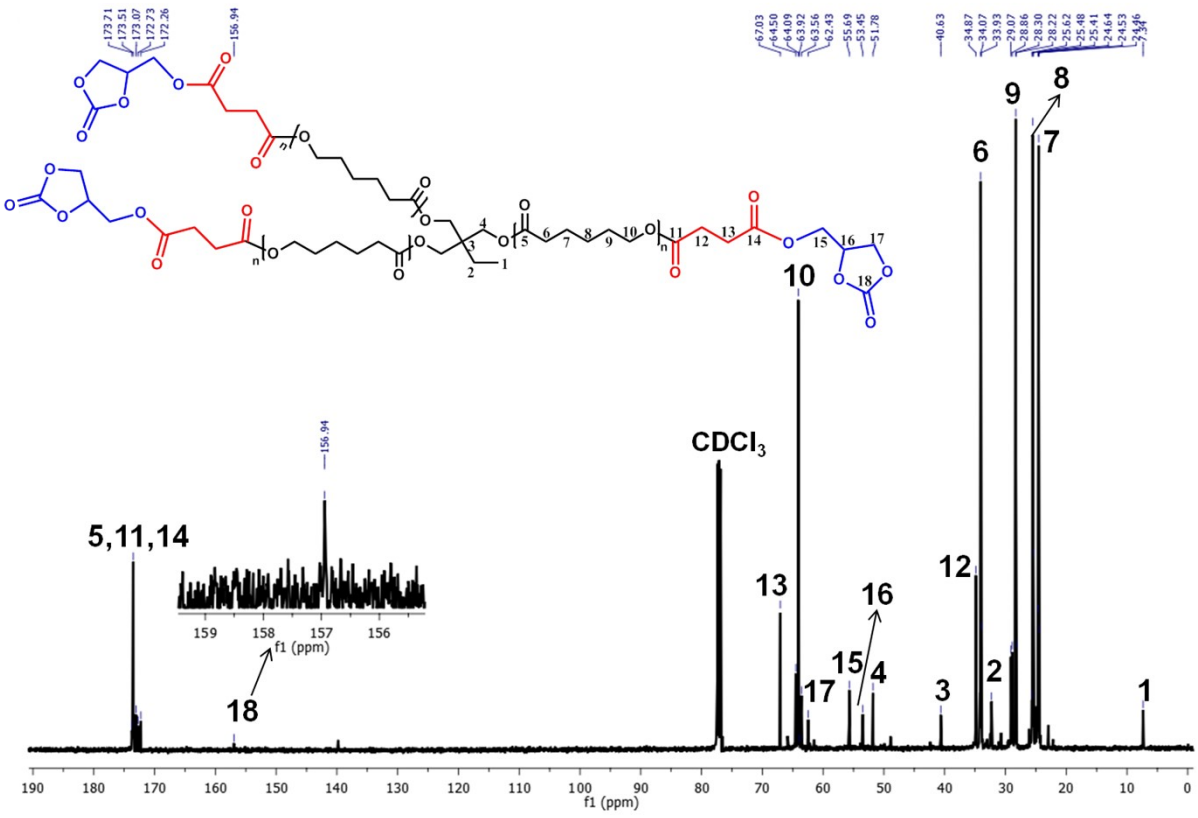


Figure S7. ^{13}C NMR of glycerol carbonate derivative of PCL, PCL-(COOGC)$_3$.

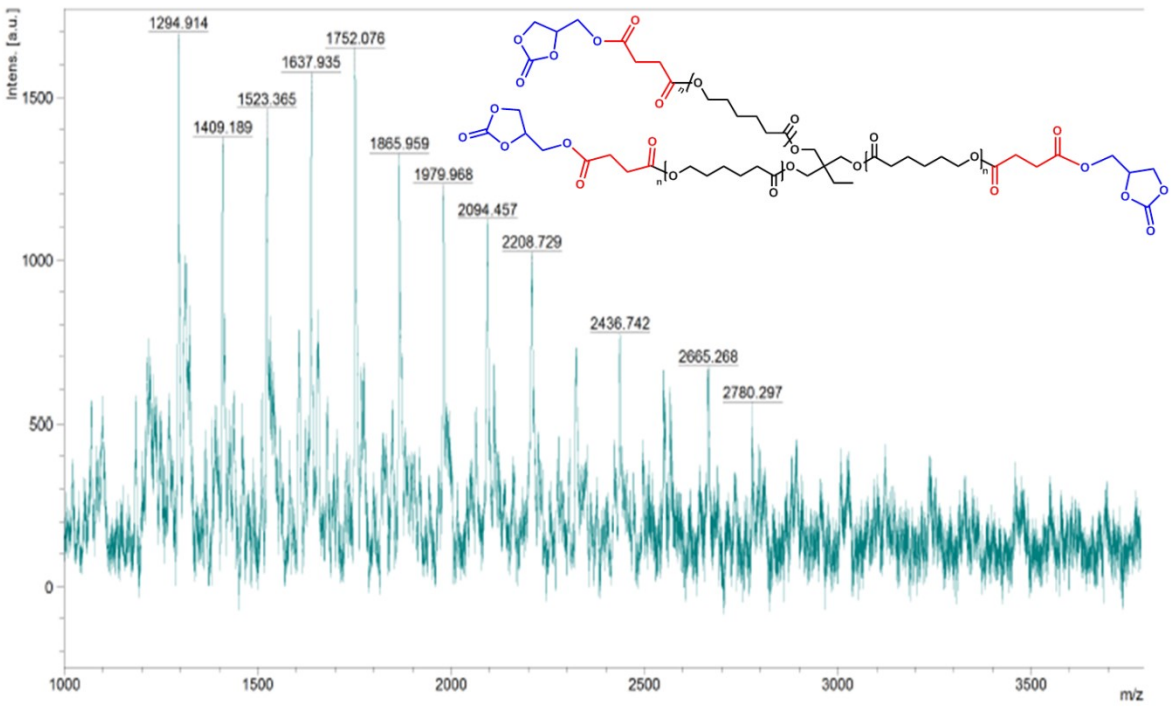


Figure S8. MALDI-TOF data of glycerol carbonate derivative of PCL, PCL-$(COOGC)_3$.

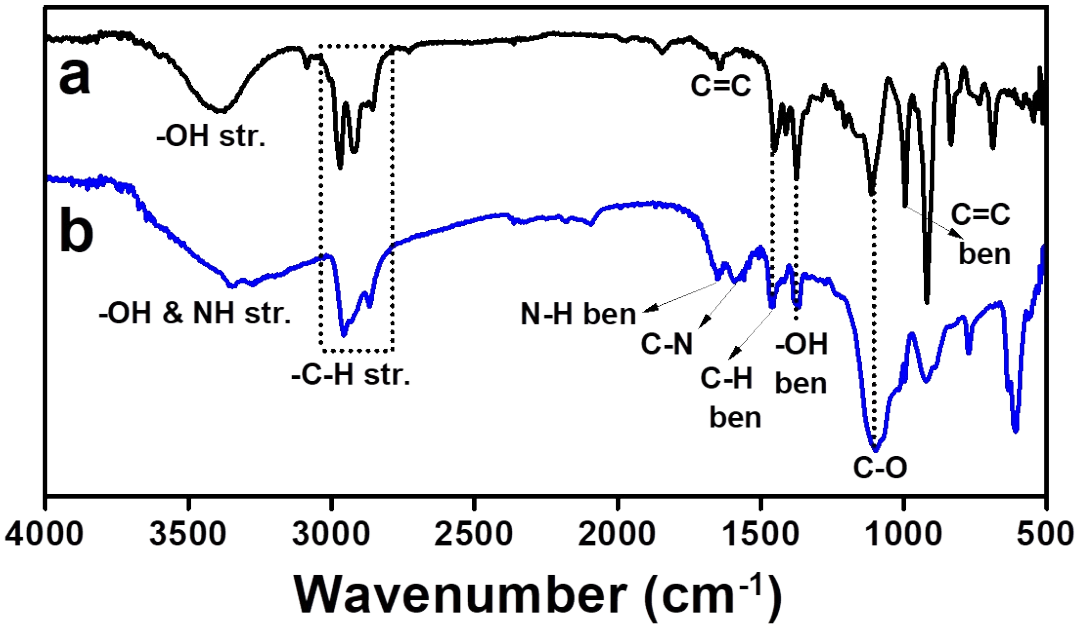


Figure S9. FT IR data of a) linalool and b) LLDA.

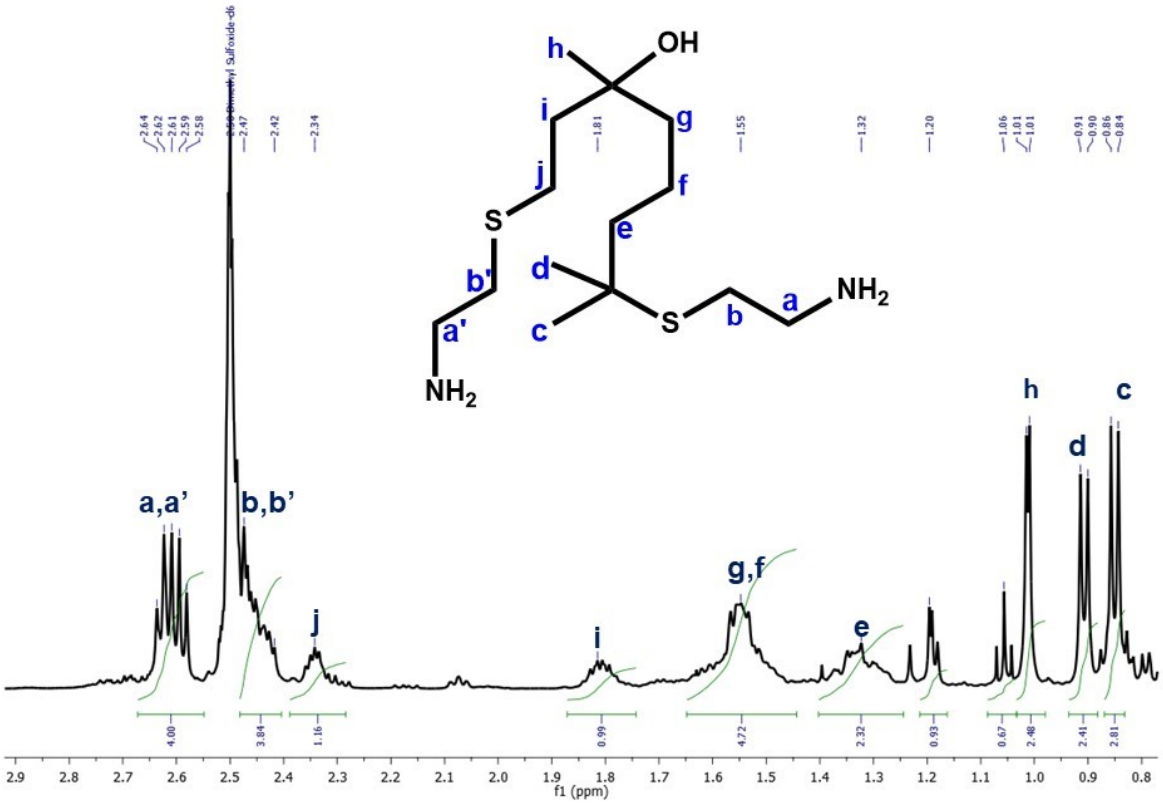


Figure S10. [1]H-NMR spectrum of linalool diamine (LLDA).

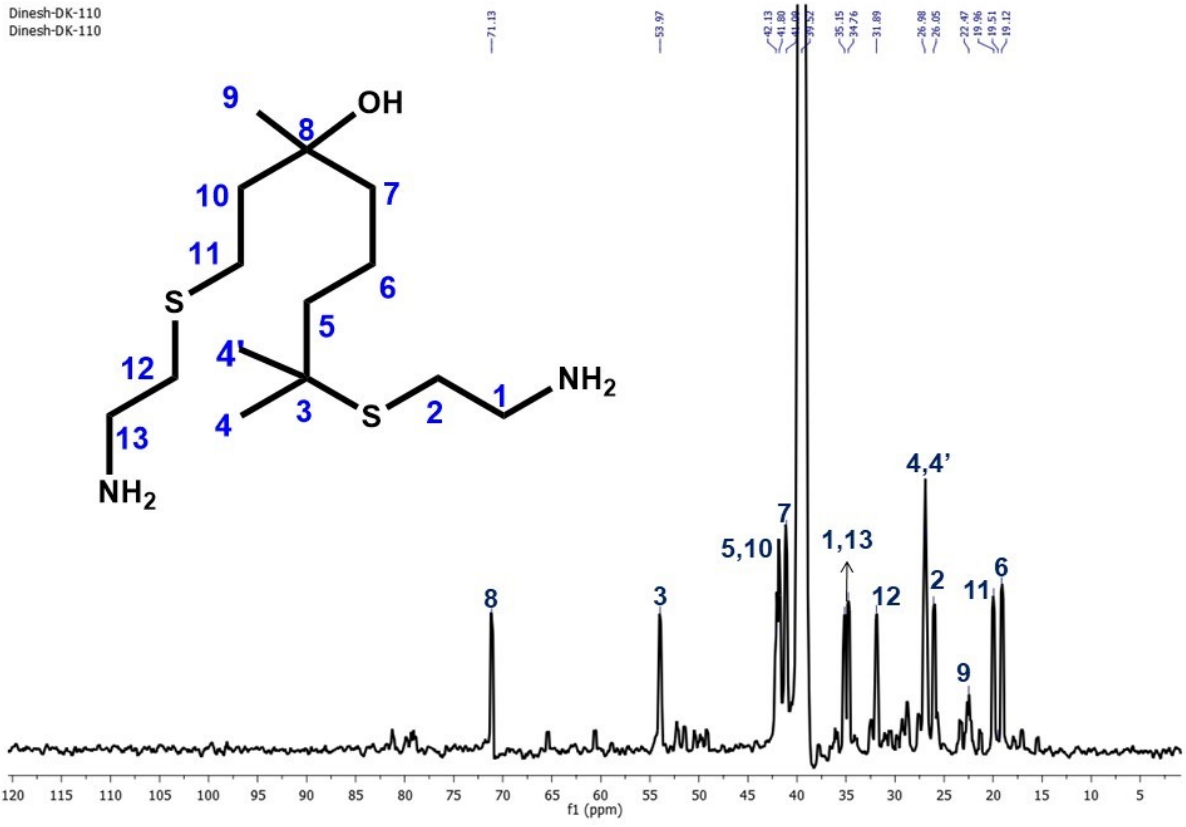


Figure S11. [13]C-NMR spectrum of linalool diamine (LLDA).

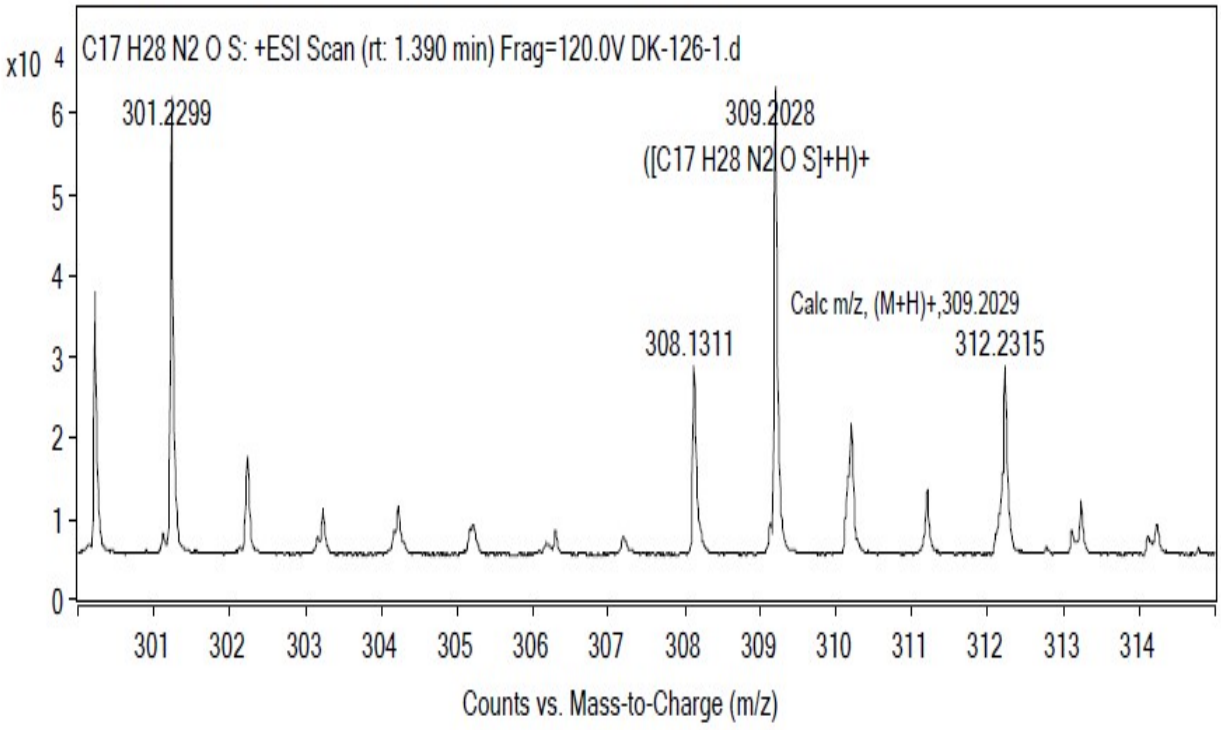


Figure S12. HR-MS data of linalool diamine (LLDA).

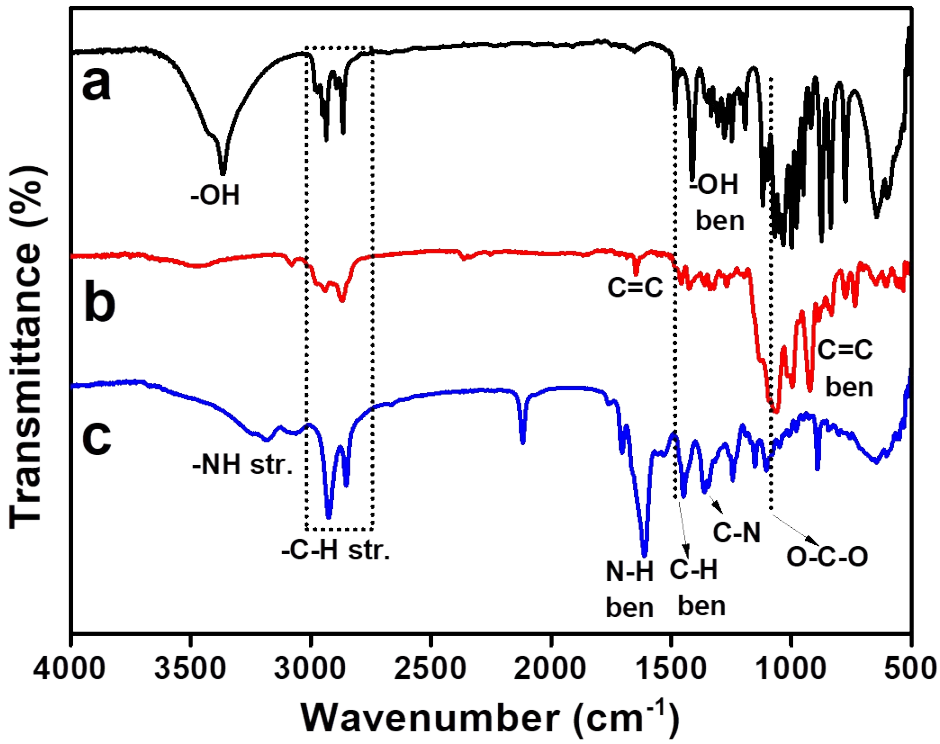


Figure S13. FT IR data of a) ISOOH, b) ISOAE and c) ISODA.

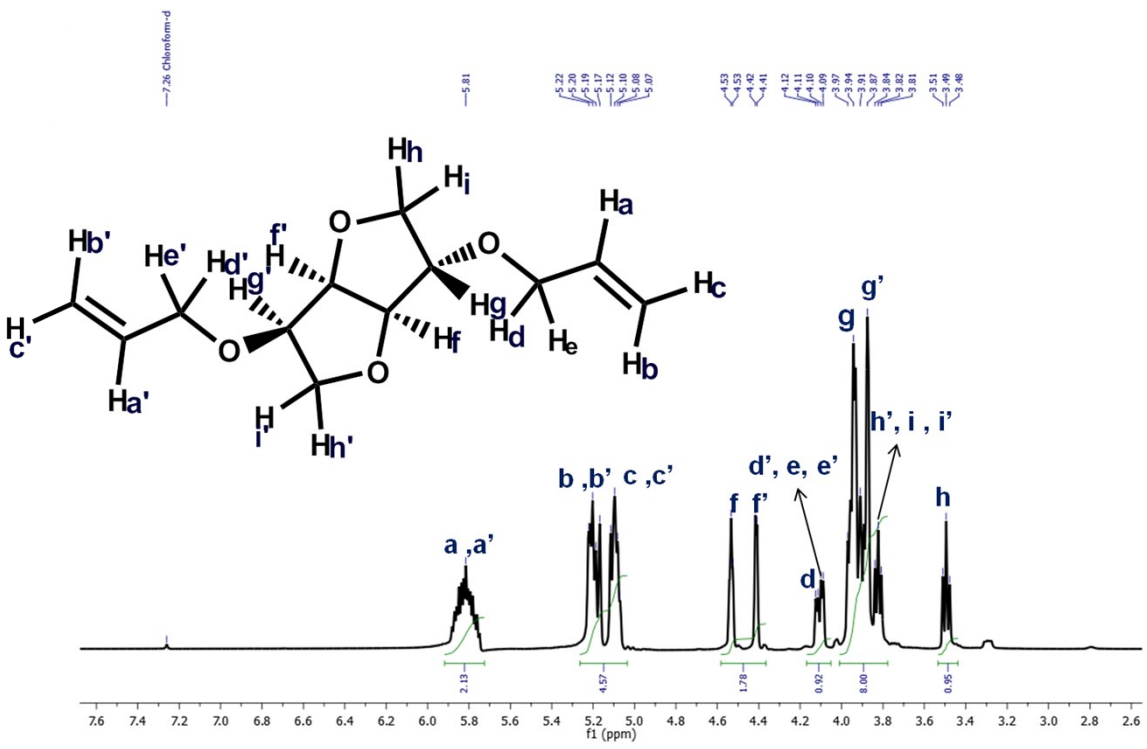


Figure S14. [1]H NMR spectrum of isosorbide allyl ether (ISOAE).

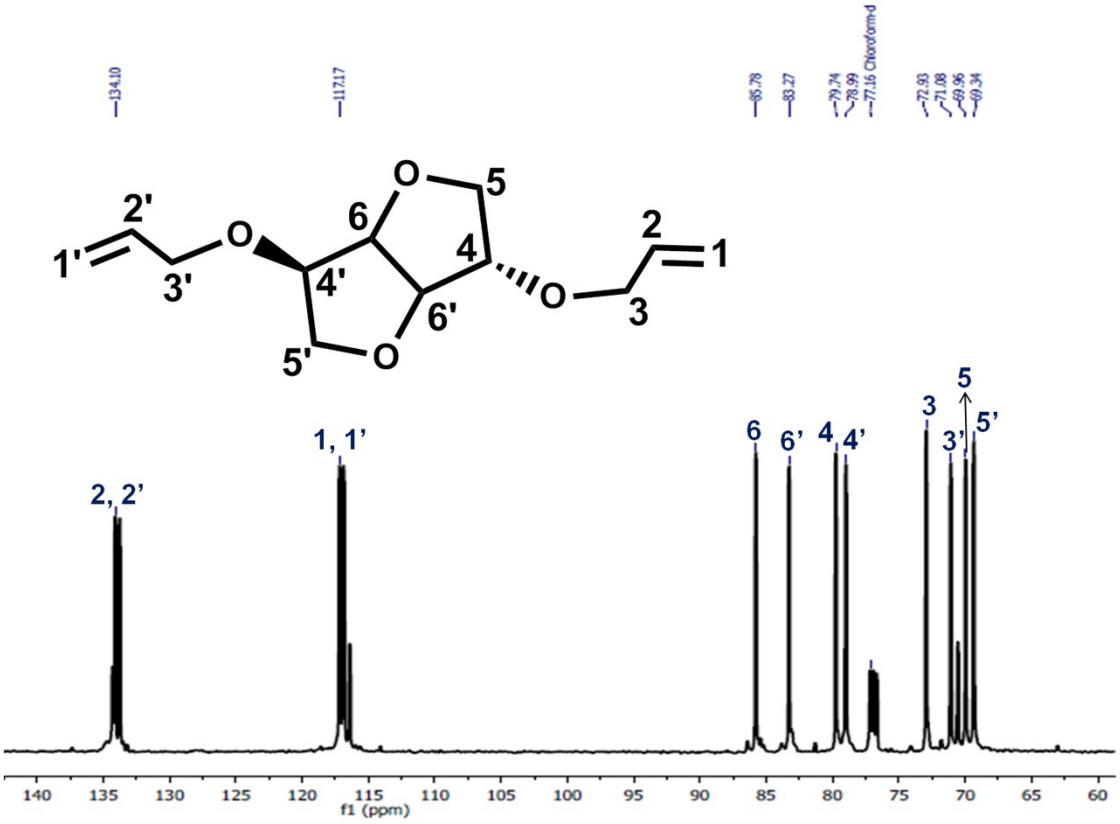


Figure S15. [13]C NMR spectrum of isosorbide allyl ether (ISOAE).

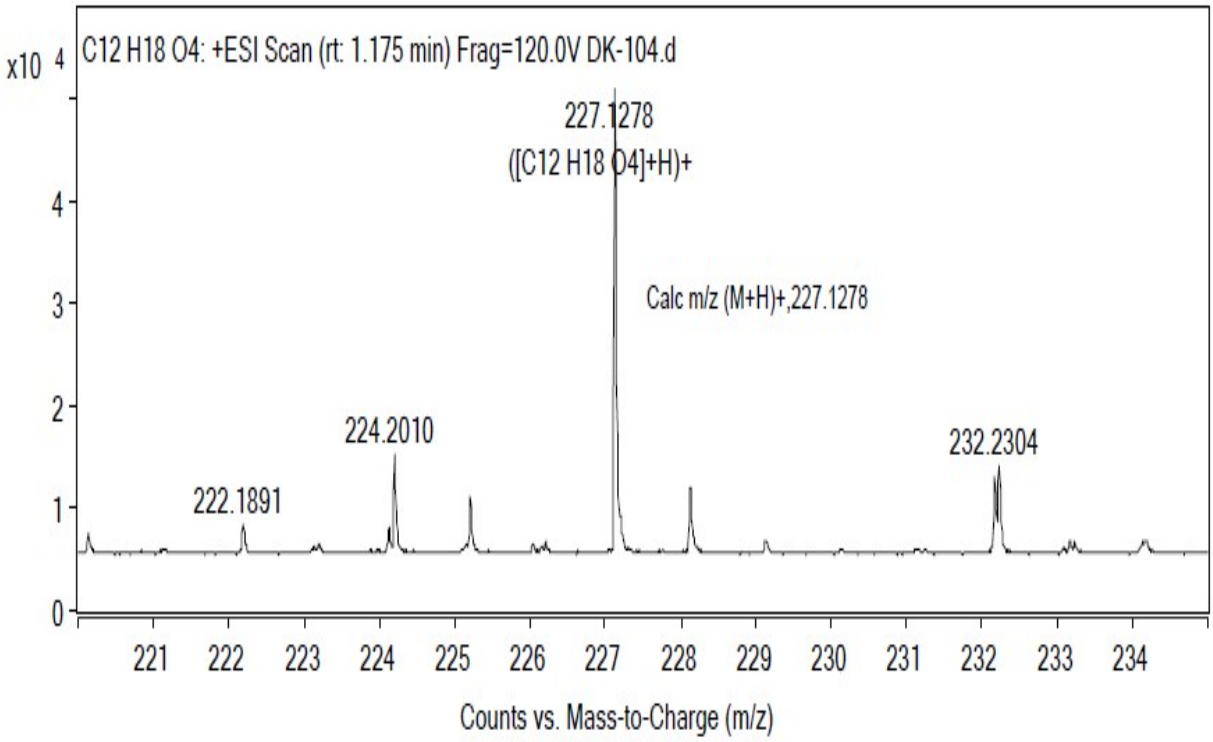


Figure S16. HR-MS data of ISOAE.

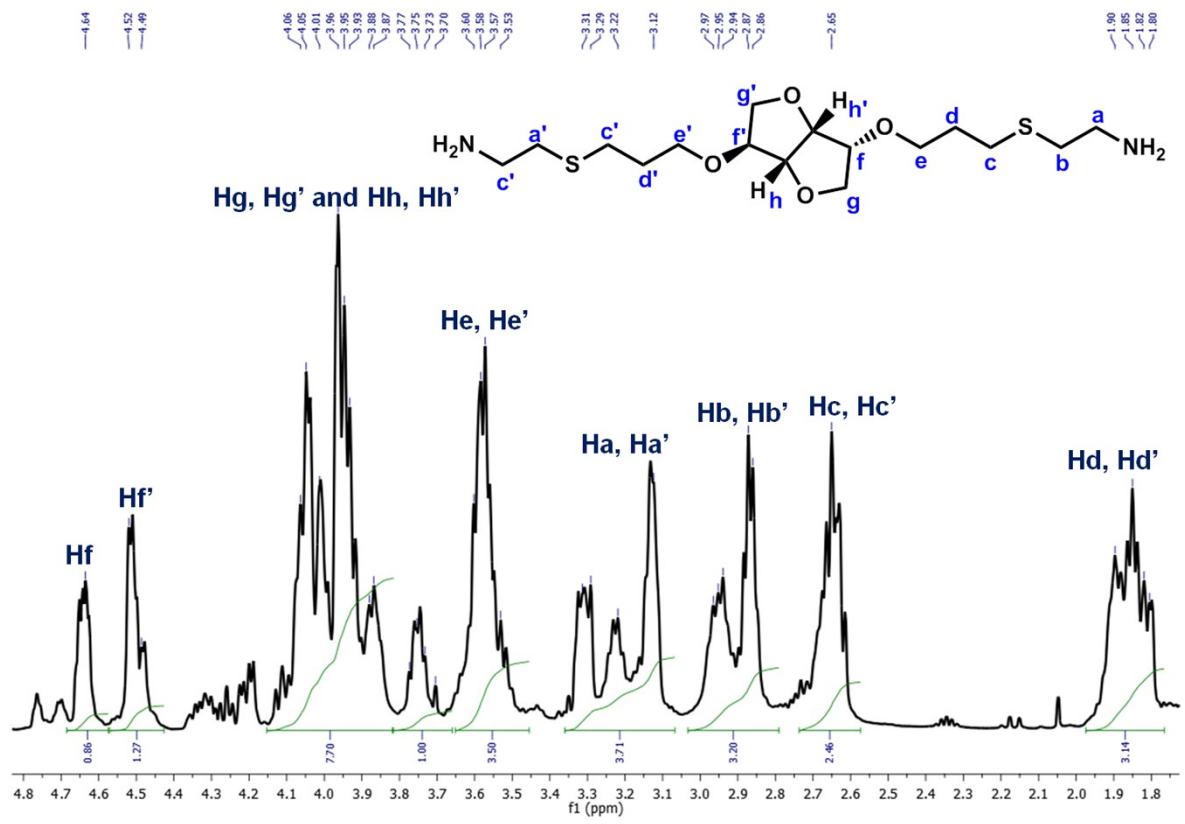


Figure S17. ^{1}H NMR spectrum of ISODA.

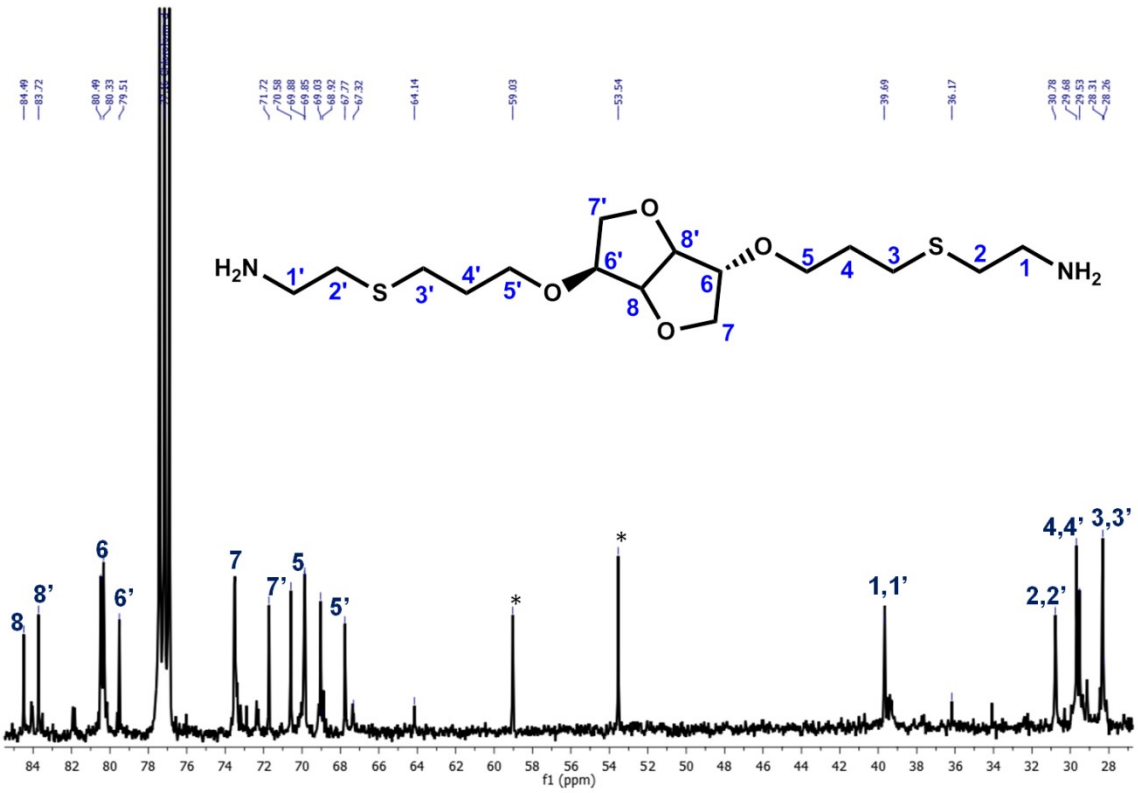


Figure S18. ^{13}C NMR spectrum of ISODA.

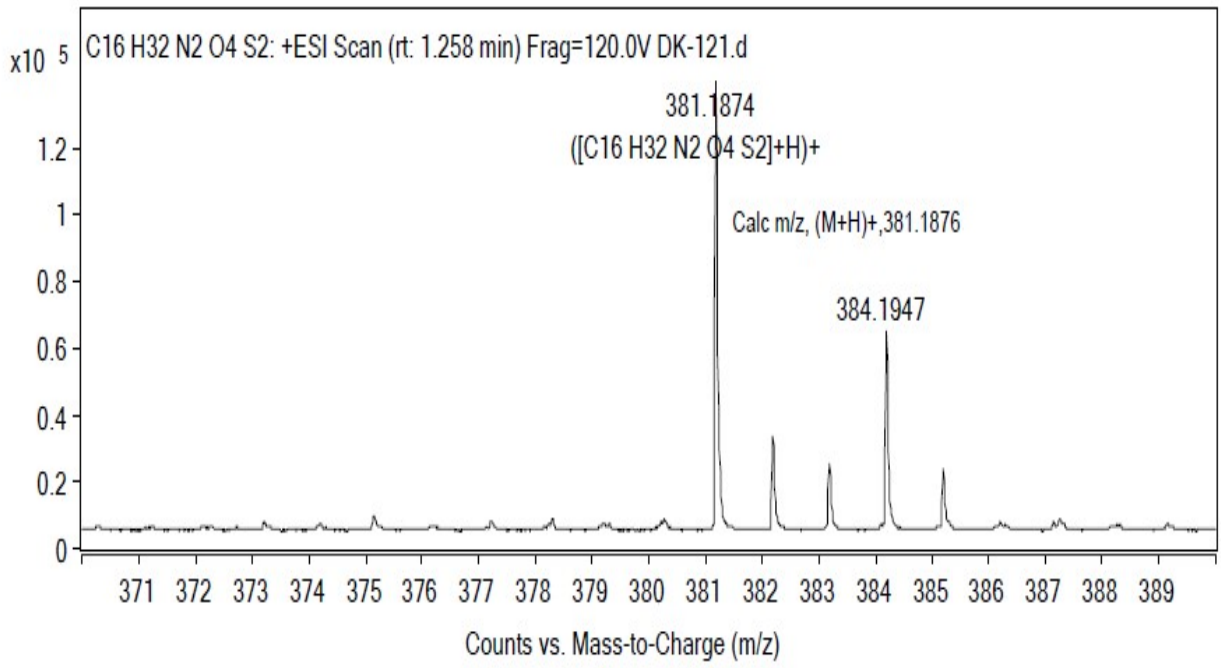


Figure S19. HR-MS data of ISODA.

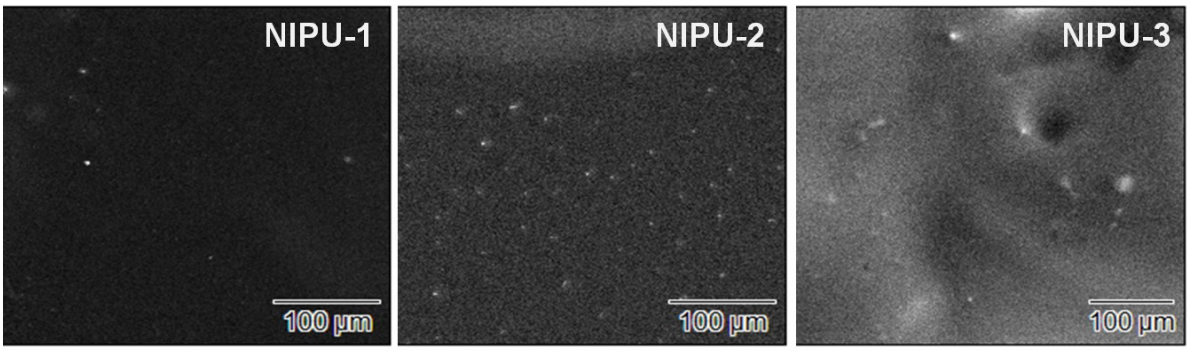


Figure S20. SEM images of PU-1, PU-2 and PU-3 films.

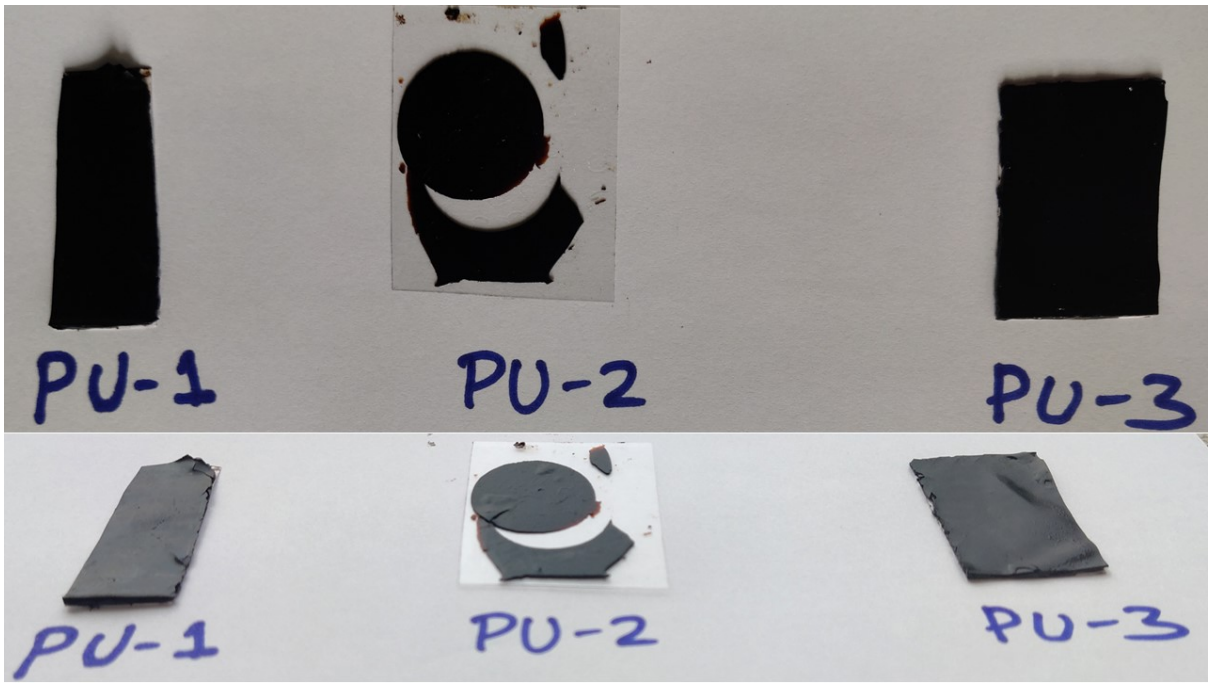


Figure S21. Physical appearance of films, PU-1, PU-2 and PU-3 [6-9].

Table S2. Remaining wt.% of PU samples after the degradation study over 50 days

Degradation period in days	**5th**	**15th**	**25th**	**50th**
PU films	**Remaining wt.%**			
PU-1	85.52	80.69	77.94	75.87
PU-2	92.15	89.22	88.24	83.34
PU-3	98.67	94.67	92.00	73.34

Table S3. Composition of elements for PU-1, PU-2 and PU-3

PU films	C (atom %)	N (atom %)	O (atom %)	S (atom %)
PU-1	42.99	14.40	42.61	-
PU-2	49.12	13.19	37.64	0.05
PU-3	29.72	6.81	63.00	0.47

Detailed procedure for water swelling/moisture sorption analysis

1. PU film sample (100 mg) was loaded in glass vial and added with distilled water (5 ml) prior to incubation at ambient condition for 24 h [10].

2. The soaked PU film was wiped off by tissue paper to eliminate excess water after 24 h gently, prior to the measurement of sample weight and substituted into the formula given below.

$Moisture\ sorption\ (\%) = (w_{moist} — w_{original})/w_{original} \times 100$

3. The above experimental protocol was executed consecutively for the period of 14 days. Since the results remains same even after measured till fourteenth day, further measurements were not continued.

Table S4. water swelling analysis data for the period of two weeks

Sample	1st Day	2nd Day	3rd Day	4th Day	5th Day	6th Day	7th Day	After 14th Day
NIPU-1	13.59%	16.00%	23.68%	28.94%	36.40%	23.68%	23.65%	23.65%
NIPU-2	23.27%	7.54%	28.93%	27.04%	28.93%	27.67%	27.67%	27.67%
NIPU-3	5.76%	5.76%	5.76%	5.76%	5.76%	5.76%	5.76%	5.76%

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