Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPORTING INFORMATION

Lysinol: A Renewably Resourced Alternative to Petrochemical Polyamines and Aminoalcohols

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Supporting Information

Page

3. **Figure SI 1. ^{1}H NMR spectrum of distilled lysinol (D_2O)**
4. **Figure SI 2. ^{13}C NMR spectrum of distilled lysinol (D_2O).**
5. **Figure SI 3. HP Liquid Chromatogram of crude lysine hydrogenation solution (mass spec detection).**
6. **Figure SI 4. Summed mass spectrum (1.24-5.27 min) of the crude lysinol liquid chromatogram shown in Figure SI 3.**
7. **Figure SI 5. Distilled lysinol mass spectrum.**
8. **Figure SI 6. Gas chromatogram (FID detection) of crude reaction product resulting from lysine hydrogenation.**
9. **Figure SI 7. Gas chromatogram (FID detection) of distilled lysinol.**
10. **Figure SI-8: ^{1}H NMR of lysine hydrogenation solutions showing the product distributions obtained at various temperatures.**
11. **Figure SI-9. ^{19}F NMR peak deconvolution of lysinol bis-Mosher amide prepared from racemic lysinol (hydrogenation of racemic lysine) and S-Mosher acid chloride.**
12. **Figure SI-10. ^{19}F NMR peak deconvolution of lysinol bis-Mosher amide prepared from R-lysinol (hydrogenation of R- lysine) and S-Mosher acid chloride (RRR major diastereomer, RSR minor diastereomer).**
13. **Figure SI 11: Lysine conversion and lysinol yield during catalyst recycle study.**
14. **Preparation and Evaluation of Epoxy Thermosets.**

Figure SI 1. ^{1}H NMR spectrum of distilled lysinol (D_2O).

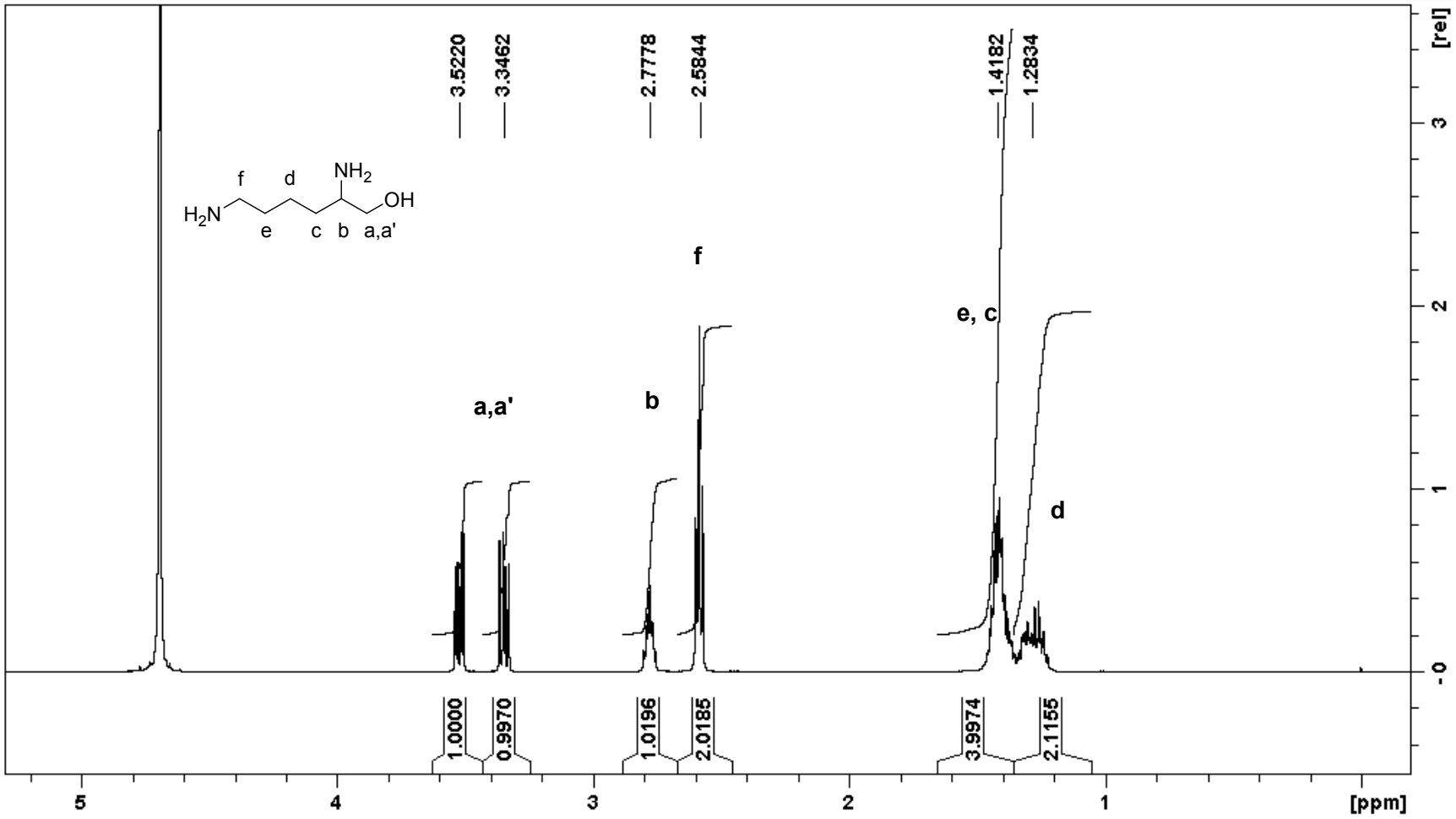


Figure SI 2. ^{13}C NMR spectrum of distilled lysinol (D_2O).

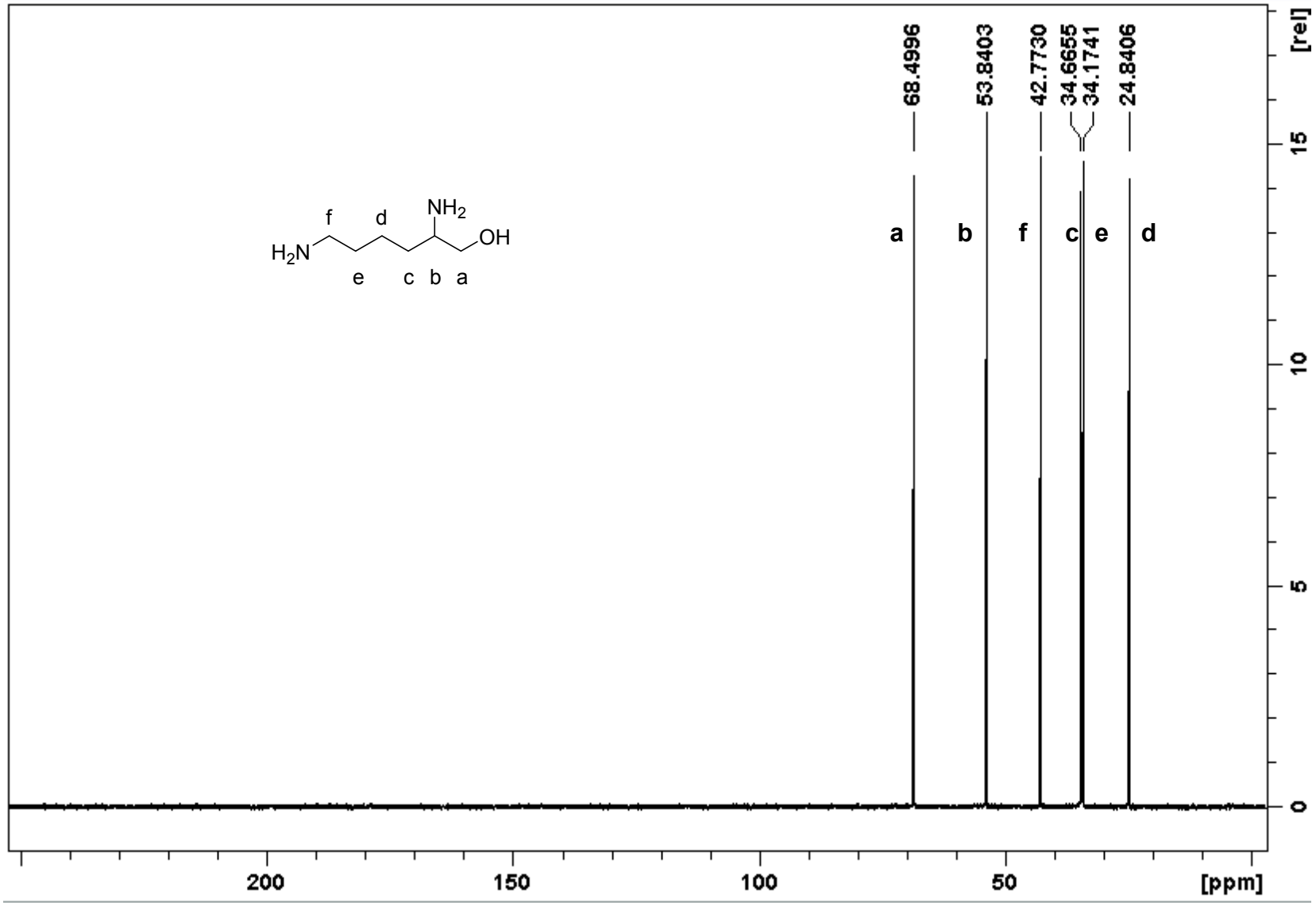
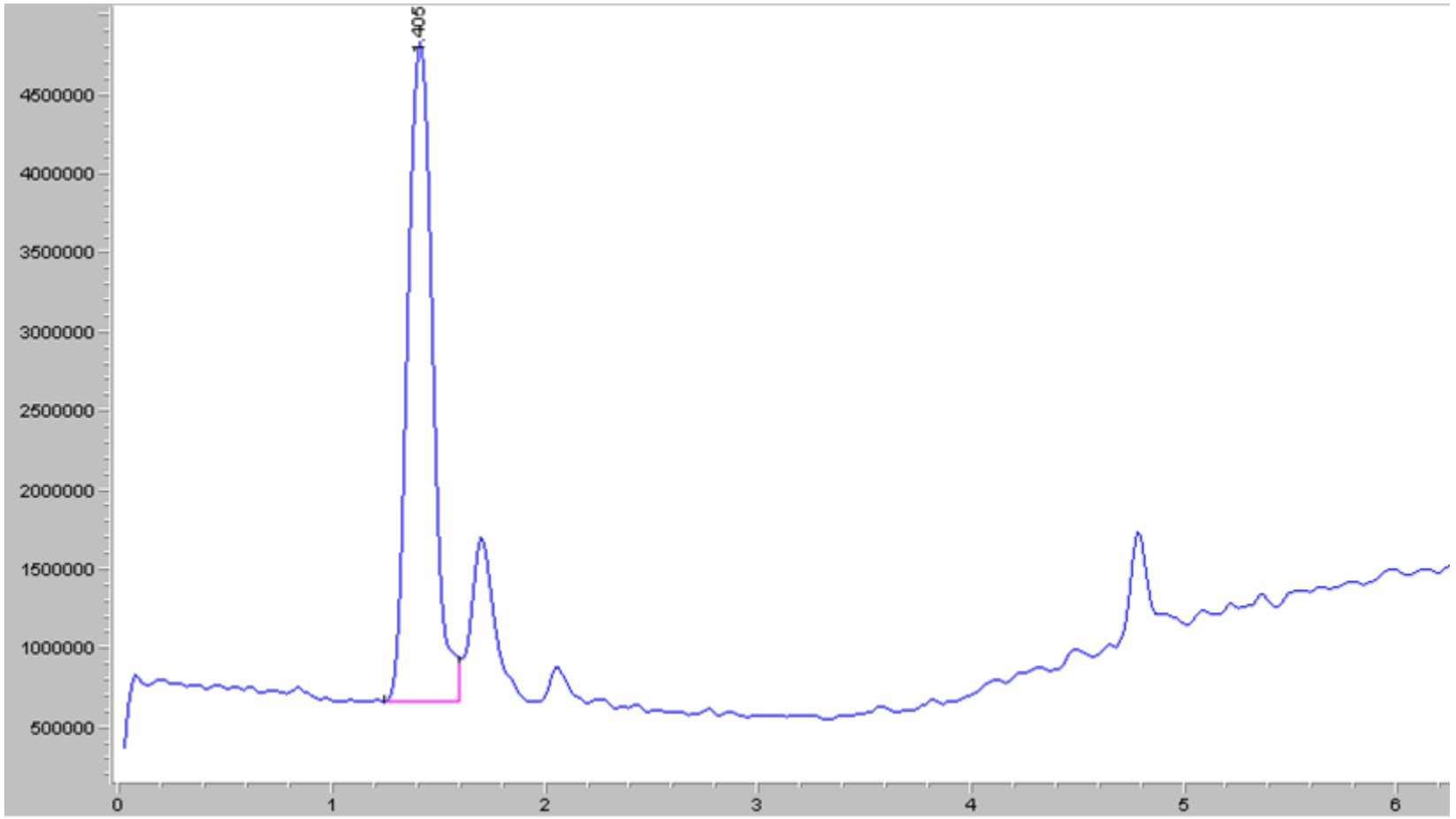
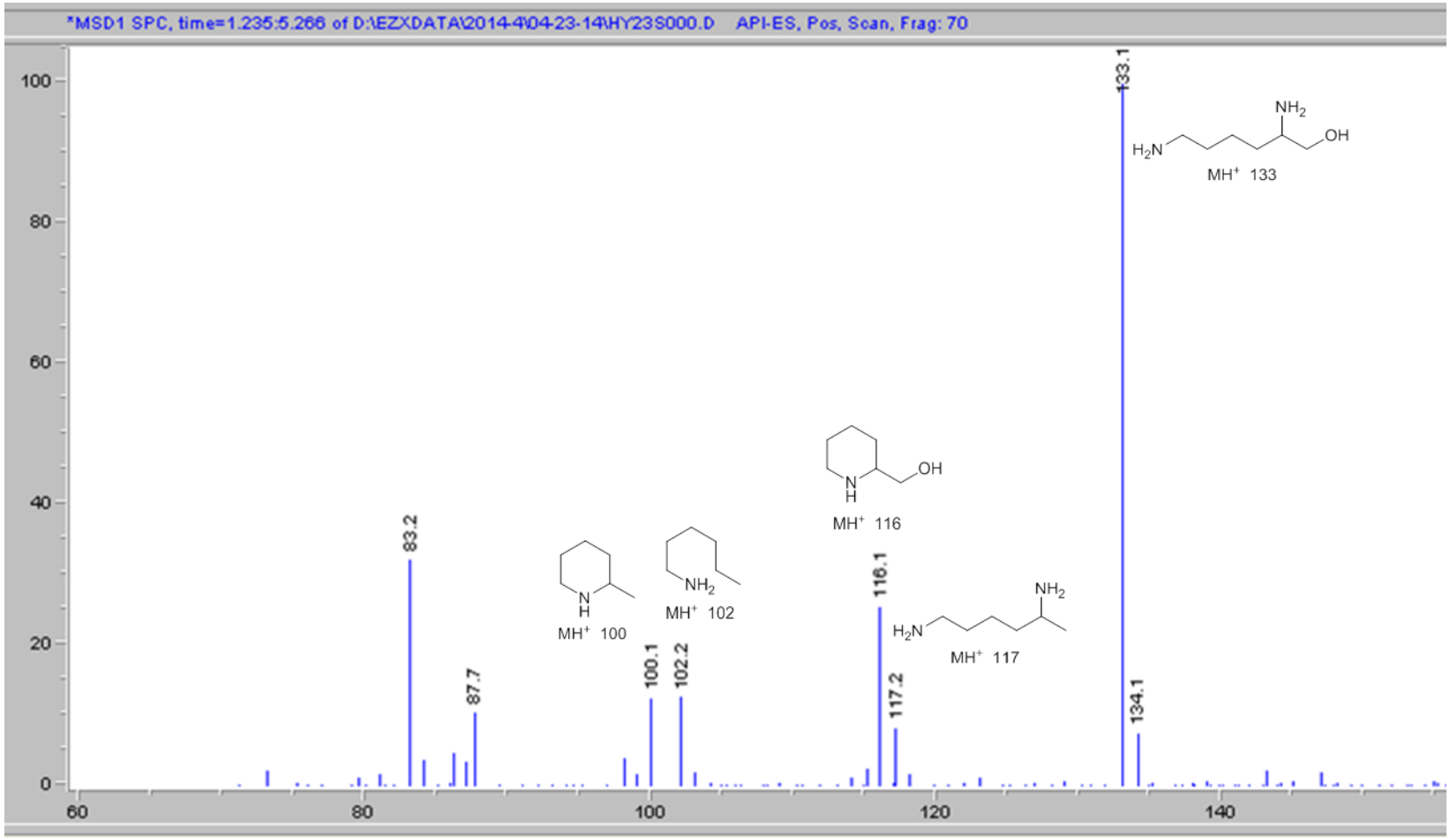


Figure SI 3. HP Liquid Chromatogram of crude lysine hydrogenation solution (MS detection).



Hydrogenation conditions: 14 wt % aqueous L-lysine, 1.0 equiv H_2SO_4, 3.4 wt % Ru/C catalyst, 68.9 bar H_2, 100 °C. Upon completion of the hydrogenation and aliquot was removed from the reaction solution, filtered to remove catalyst, diluted with water, and injected on the HPLC. HPLC (Hewlett-Packard 1100) was performed a mass spectrum detector. The separation was carried out on a Zorbax Eclipse AAA column (4.6 x 150 mm) operating at a flow rate of 1 mL/min at 60 °C. The mobile phase consisted of a mixture of water and 0.1% formic acid (Phase A) and acetonitrile and 0.1% formic acid (Phase B) at a gradient of 95% A/5 %B to 0% A/100 %B over 10 min, followed by a 4 min hold.

Figure SI 4. Summed mass spectrum (1.24-5.27 min) of the crude lysinol liquid chromatogram shown in Figure SI 3.



Hydrogenation conditions: 14 wt % aqueous L-lysine, 1.0 equiv H_2SO_4, 3.4 wt % Ru/C catalyst, 68.9 bar H_2, 100 °C. Upon completion of the hydrogenation an aliquot was removed from the reaction solution, filtered to remove catalyst, diluted with water, and injected on the HPLC.

Figure SI 5. Distilled lysinol mass spectrum.

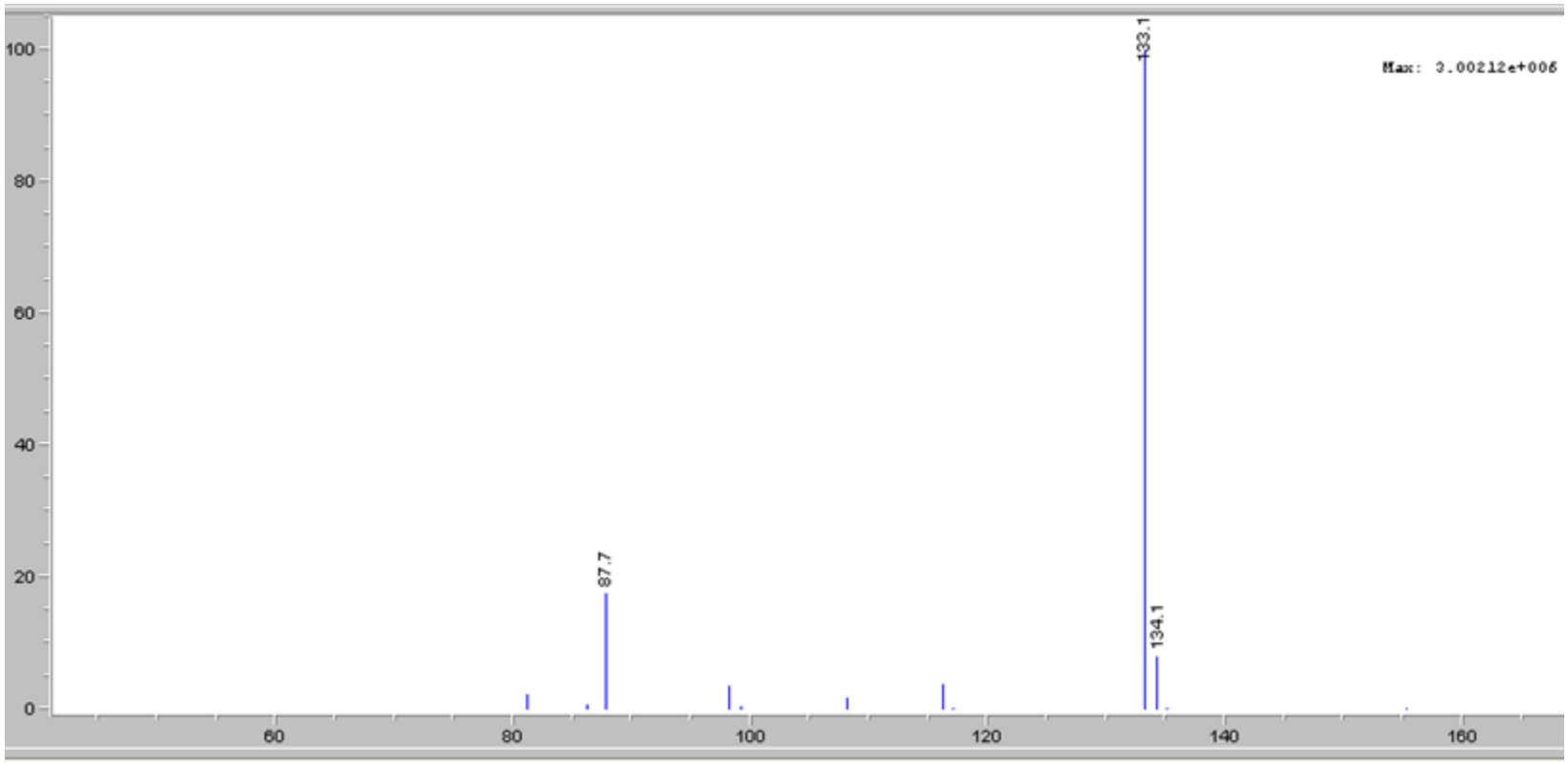
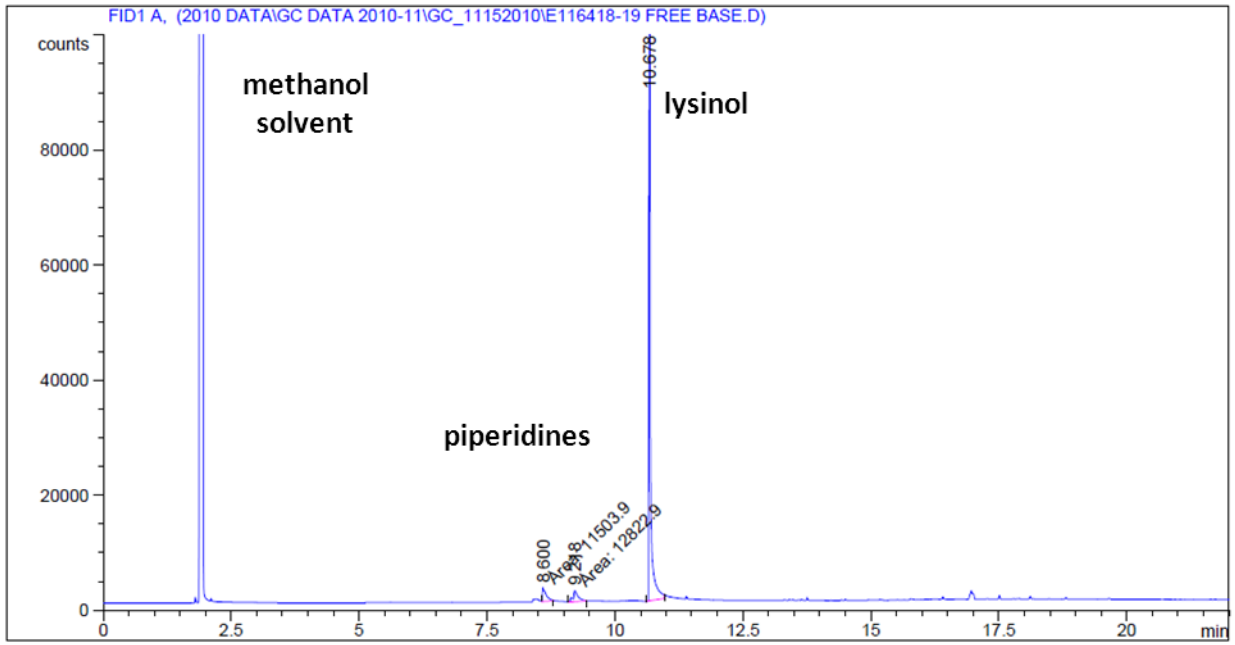


Figure SI 6. Gas chromatogram (FID detection) of crude reaction product resulting from lysine hydrogenation.

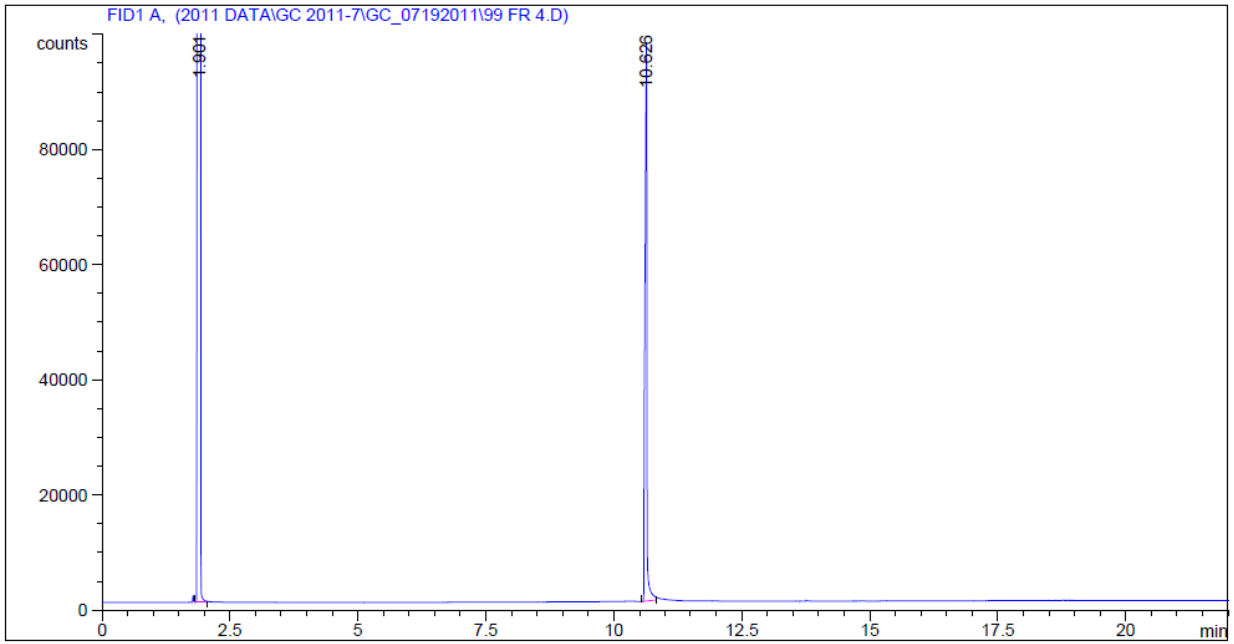


Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	8.600	MM	0.0812	1.15039e4	2361.74048	4.62847
2	9.218	MM	0.1085	1.28229e4	1968.89771	5.15916
3	10.678	BB	0.0441	2.24220e5	9.31191e4	90.21237
Totals :				2.48547e5	9.74497e4	

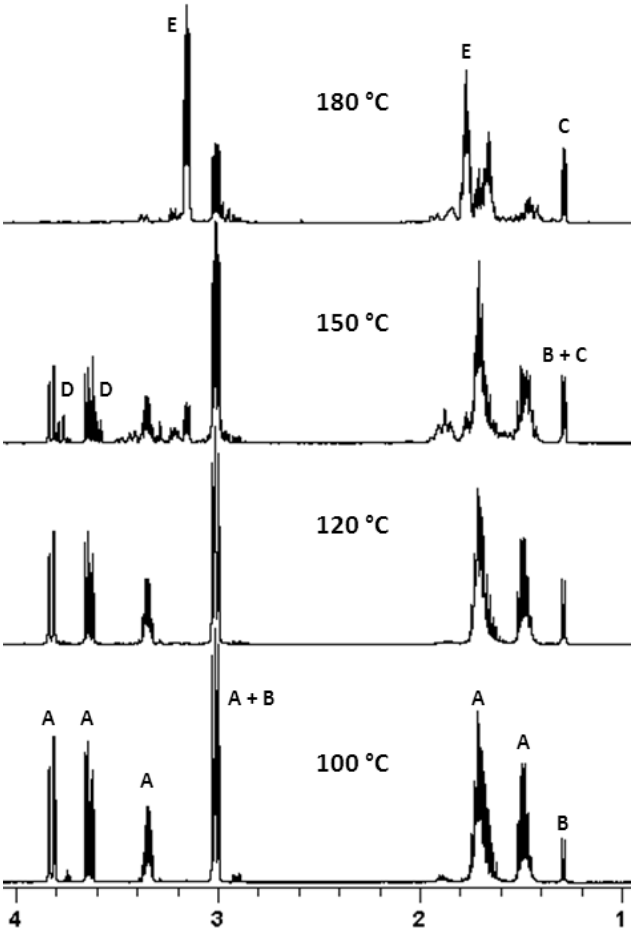
Hydrogenation conditions: 15 wt % aqueous L-lysine, 2.07 equiv H_3PO_4, 1.3 wt % Ru/C catalyst, 68.9 bar H_2, 120 °C. Upon completion of the hydrogenation an aliquot was removed from the reaction solution, filtered to remove catalyst, and the pH adjusted to ca. 12 with NaOH. The sample was then diluted with methanol and injected on the GC. Gas chromatography performed with a Hewlett-Packard 5890 with FID detection and a 30 m x 0.32 mm x 0.25 μm ZB-5 column. Sample injections were made at a 40 °C initial column temperature and after a 4 min hold were ramped to 300 °C at 20 $^{o}C\ min^{-1}$.

Figure SI 7. Gas chromatogram (FID detection) of distilled lysinol.



Gas chromatography performed with a Hewlett-Packard 5890 with FID detection and a 30 m x 0.32 mm x 0.25 µm ZB-5 column. Sample injections were made at a 40 °C initial column temperature and after a 4 min hold were ramped to 300 °C at 20 ^{o}C min^{-1}.

Figure SI-8: ^{1}H NMR of lysine hydrogenation solutions showing the product distributions obtained at various temperatures.



Experimental conditions: 14 wt.% aqueous L-lysine, 1.0 equiv H_2SO_4, 3.4 wt % Ru/C catalyst, 68.9 bar H_2, temperature as indicated. Reaction time – 24h for all the runs except at 100°C run (45h).. Aliquots were removed from the reactor after hydrogenation, filtered to remove trace catalyst, diluted with D_2O and the ^{1}H NMR spectra recorded. Assignment of major diagnostic peaks: A, lysinol; B, 1,5-diaminohexane; C, 2-methylpiperidine; D, 2-hydroxymethylpiperidine; E, piperidine. Trace amounts of unreacted lysine may be observed at 3.74 ppm. Resonances at 2.9 and 1.9 ppm are due to $TMS(CH_2)_3SO_3Na$ internal standard.

Figure SI-9. ^{19}F NMR peak deconvolution of lysinol bis-Mosher amide prepared from racemic lysinol (hydrogenation of racemic lysine) and S-Mosher acid chloride.

52-46 % RRR; 48-54 % RSR;

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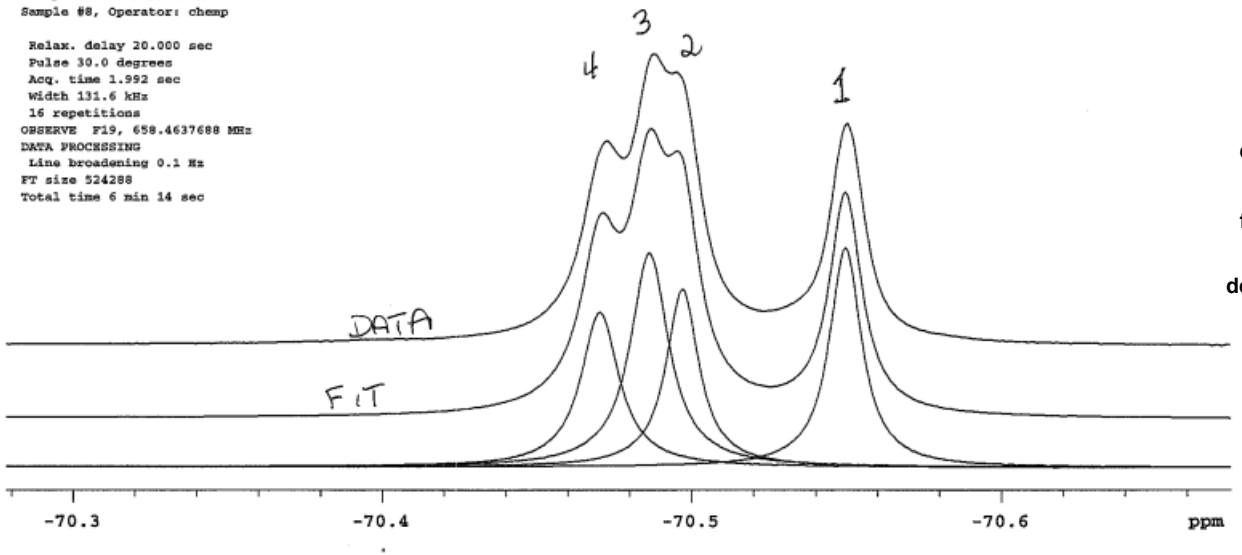
[illegible]FIT, AUTOMATIC PLOT
Agilent 700 NMR
Probe: 5mm_HFC Samplename: 987618
TOP: ACTUAL SPECTRUM
[illegible] FIT
BOTTOM: INDIVIDUAL COMPONENT PLOTS
Data Collected on:
V700nmrhost-vnmrs700
Archive directory:
/home/data2/500NMRgroup/Moloy
Sample directory:
987618
FidFile: 987618_PRESAT_20120301_801

Pulse Sequence: PRESAT
Solvent: cd2cl2
Data collected on: Mar 1 2012

Temp. 25.0 C / 298.1 K
Sample #8, Operator: chemp

Relax. delay 20.000 sec
Pulse 30.0 degrees
Acq. time 1.992 sec
Width 131.6 kHz
16 repetitions
OBSERVE F19, 658.4637688 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 524288
Total time 6 min 14 sec

LINE	FREQ (Hz)	HEIGHT	WIDTH (Hz)	GAUSS FR.	INTEGRAL
1	-46454.50	45.08	8.20	0.000	580.67
2	-46419.90	36.49	8.35	0.000	478.72
3	-46413.20	43.91	9.78	0.000	674.83
4	-46402.60	31.76	9.76	0.000	487.07

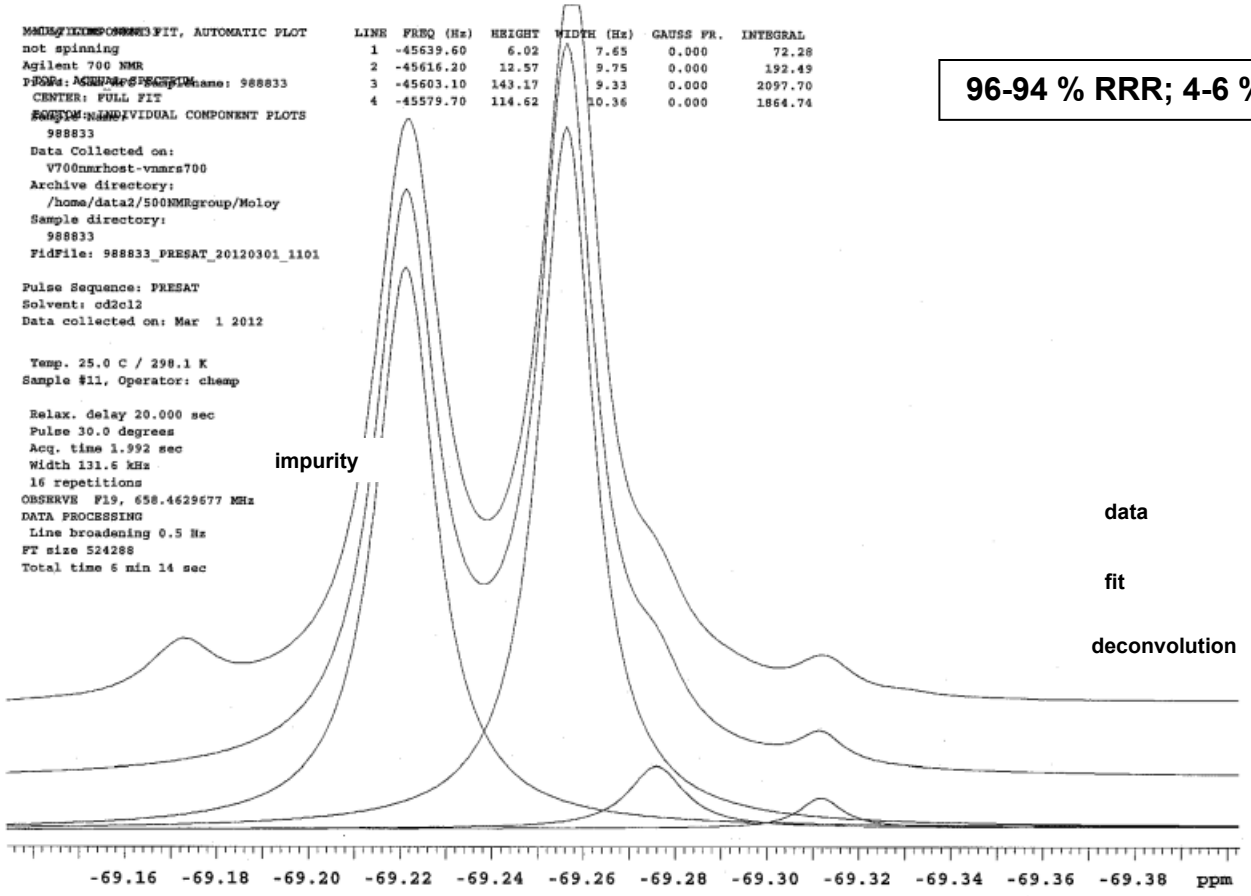


data

fit

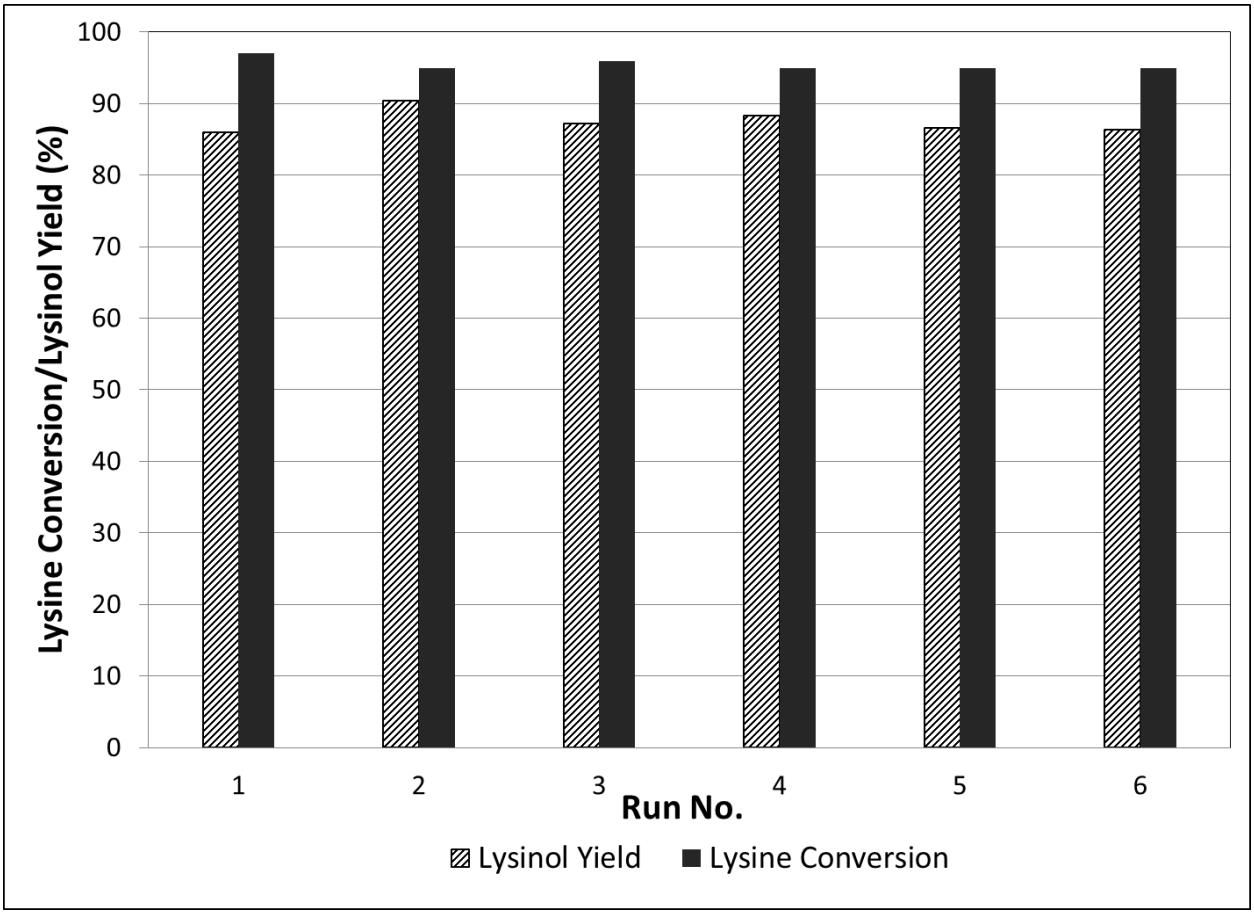
deconvolution

Figure SI-10. ^{19}F NMR peak deconvolution of lysinol bis-Mosher amide prepared from R-lysinol (hydrogenation of R-lysine) and S-Mosher acid chloride (RRR major diastereomer, RSR minor diastereomer).



96-94 % RRR; 4-6 % RSR; 92-88 % ee

Figure SI 11: Lysine conversion and lysinol yield during catalyst recycle study



Experimental conditions: Feed: 30 g of 10% Lysine free base (Sigma), ~83% water, ~7% H_2SO_4, pH =1.7, Catalyst: 1 g 5% Ru/C catalyst (Sigma), Temperature – 120 ^oC, Reaction time – 16hr, H_2 pressure – 65 bar.

Catalyst Lifetime/Recycle Study

These data were generated by performing batch hydrogenation reactions using a fresh lysine/H_2SO_4 charge and recycling the catalyst. After each hydrogenation the catalyst was isolated by filtration, washed with water, dried, and returned to the reactor. ICP analyses of the filtrate solutions showed no detectable ruthenium in these samples (1 ppm detection limit). Analysis of the filtrate from a single hydrogenation experiment performed at ca. 14 wt% lysine/10 wt% H_2SO_4 showed 2.5 ppm Ru.

For a commercial process, one would need to consider a continuous process (in CSTR) and catalyst lifetime studies should be carried out over a month or more. However, this was not the focus of this work and should be considered separately.

Preparation and Evaluation of Epoxy Thermosets

Determination of Epoxide (EEW) and Amine (AEW) Equivalent Weight

To achieve the correct stoichiometric balance of epoxy resin and amine hardener the EEW and AEW must be known. Samples of BADGE obtained from Aldrich (poly(bisphenol A-co-epichlorohydrin), gyclidyl end-capped, catalogue number 405493) and Dow (D.E.R. 331) were analyzed by ^{1}H NMR (CD_2Cl_2) and careful integration used to calculate the degree of oligomerization. Molecular weights by this method were found to be approximately 373, giving an EEW (molecular weight/number of epoxy groups) of 186.

The lysinol and DETA were pure samples prepared in this laboratory or purchased from Aldrich. Therefore, the AEWs (molecular weight/number of N-H groups) for lysinol and DETA are 33.05 and 20.63, respectively, and these values were used in this study.

Nanoindentation

The samples were prepared by combining the appropriate amounts of epoxy and amine to give a 1:1 stoichiometry of epoxide to N-H groups (EEW/AEW = 2), stirring thoroughly for 2 minutes, and then pouring the mixture into aluminum weighing dishes (5 cm diameter) to a depth of ca. 5 mm. The material was allowed to stand at ambient temperature for 18 h, whereupon it hardened to a tack-free, colorless solid. The sample was cured for 3 h in a 100 ^{o}C oven, cooled, the aluminum dish was carefully peeled away from the solid thermoset, and the sample was evaluated with the nanoindenter to determine the reduced modulus and hardness.

Tensile properties

Tensile bars and their evaluation were performed in general accordance with ASTM International test method D1708-13.[1] "Dogbone" test specimens were prepared by cutting a

properly shaped mold from clay or silicone using a specimen die. Sample fabrication by directly cutting the test specimen from the cured thermoset was not possible due to sample brittleness and subsequent cracking. The appropriate amounts of epoxy and amine (EEW/AEW = 2) were combined in a plastic beaker, hand mixed thoroughly, and then poured into the molds. After standing overnight at ambient temperature the samples were heated in an oven at 65 ^{o}C for 30 min. The cured samples were removed from the molds and then evaluated.

Lap shear testing

Test samples for adhesive strength lap shear testing were prepared in general accordance with ASTM International test method D1002-10.[2] The single-joint lap joint specimens were fabricated from stainless steel, each measuring 25.4 mm by 154 mm and 1.42 mm thickness. The overlap length was 25.4 mm to give a total overlap area of 645 mm^2. The test joints were prepared by sanding a region of each specimen ca. 40 mm from one end with 400 grit sandpaper. The sanded region was rinsed with water and acetone and then gently rubbed with an acetone soaked paper towel to remove any debris. The proper amounts of amine and epoxy resin (EEW/AEW = 2) were weighed into a plastic beaker and mixed for 2 min. The resulting mixture was loaded into a disposable 1 mL syringe and 0.07 mL was added to the center of the designated overlap portion of one specimen. That specimen was placed in a jig and the second specimen placed on top of it to achieve the desired overlap and to hold the two specimens in correct position during curing. A 40 g mass was placed on top of the overlapping specimens and the thermoset was allowed to harden for 18 h at ambient temperature. The assembly was then placed in a 100 °C oven for 3 h to complete the cure. Each formulation was performed in triplicate.

Compression testing

Compression testing was performed in general accordance with ASTM International test method D695-10.[3] The appropriate amounts of amine and epoxy resin (EEW/AEW = 2) were combined in a plastic beaker and mixed manually for 2 min. Approximately 3.5 mL of the resulting mixture was poured into a 6 mL capped, disposable plastic syringe (12.5 mm i.d.). The syringe was stored in an upright position for 18 h at ambient temperature whereupon the contents hardened. Curing was achieved by heating the sample for 3 h at 100 °C in an oven. After cooling the syringe was carefully scored with a razor blade and peeled away from the molded cylinder of clear, colorless, and tack-free thermoset. The cylinder ends were sanded with a belt sander until flat and perpendicular to the cylinder axis. The final cylinder length to diameter ratio was approximately 2, and duplicate samples of each formulation were evaluated.

Chemical resistance[4]

Lysinol and DETA epoxy thermosets were prepared using the appropriate amounts of amine and epoxy to give a 1:1 stoichiometric ratio of N-H and epoxy groups (EEW/AEW = 2). The materials were mixed thoroughly by hand and the resulting mixture was poured into an aluminum weighing dish. After hardening at ambient temperature for 18 h the samples were cured for 3 h at 100 °C. After cooling the aluminum was peeled from the thermoset, which was then broken into irregular pieces. Individual pieces were weighed, the masses recorded, and then placed in 20 mL scintillation vials. Solvent was added to the vial sufficient to fully immerse the sample and then the vial was sealed and allowed to stand undisturbed for 28 days at ambient temperature. The sample was removed from the vial, blotted dry with a laboratory wipe, air dried for ca. 15 minutes, and then reweighed. Chemical resistance is reported as the percent mass gain.

References

(1) D1708-13. D1708-13, Standard Test Method for Tensile Properties of Plastics by Use of Microtensile Specimens. *ASTM International* [Online Early Access]. DOI: 10.1520/D1708-13. Published Online: 2013. www.astm.org.

(2) D1002-10. D1002-10, Standard Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading (Metal-to-Metal). *ASTM International* [Online Early Access]. DOI: 10.1520/D1002-10. Published Online: 2010. www.astm.org.

(3) D695-10. D695-10, Standard Test Method for Compressive Properties of Rigid Plastics. *ASTM International* [Online Early Access]. DOI: 10.1520/D0695-10. Published Online: 2010. www.astm.org.

(4) Pham, H. Q.; Marks, M. J. *Epoxy Resins, Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, Inc.: New York, 2000.