

Acetal Metathesis Polymerization (AMP): A method for synthesizing biorenewable polyacetals

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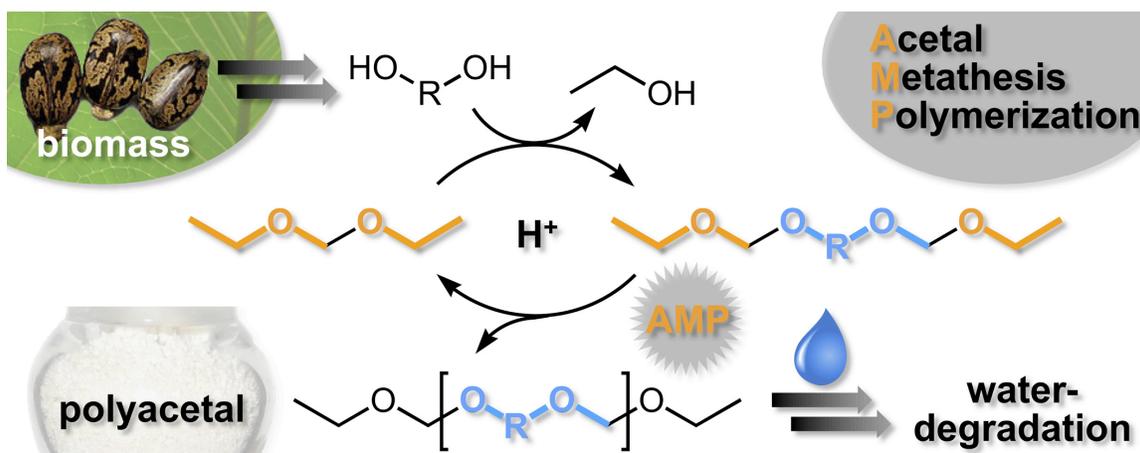
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Electronic Supplementary Information (ESI)

Supplementary Information Available: Synthetic details, analytical details, and complete polymer characterization data.

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General Considerations and Instrumentation

Unless otherwise noted, all solvents, including dimethoxymethane and diethoxymethane, were purified by stirring over calcium hydride for 24 hours and then vacuum transfer into an oven dried Straus flask containing molecular sieves. Xylenes and 1,1,2,2-tetrachloroethane were purchased from Sigma Aldrich and stored over molecular sieves. Toluene for polymerizations was dried over molecular sieves and alumina using an MBraun Solvent Purification System (MB SPS). Recrystallization solvents were purchased from Sigma Aldrich and utilized as received. The catalyst, *para*-toluenesulfonic acid (*p*-TSA), was purchased as the monohydrate from Sigma Aldrich and used as received.

CAUTION: DIMETHOXYMETHANE AND DIETHOXYMETHANE ARE HIGHLY FLAMMABLE LIQUIDS and require a high degree of care. Both substances have a flammability rating of 3 according to the Hazardous Materials Identification System (HMIS®).

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded using a Varian Mercury 300 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.0 ppm) or residual proton in the specified solvent. Coupling constants (*J*) are reported in Hertz (Hz). Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintuplet; m, multiplet; br, broad.

Differential scanning calorimetry thermograms were obtained with a DSC Q1000 from TA instruments. About 1.5-3 mg of each sample were massed and added to a sealed pan that passed through a heat/cool/heat cycle at 10 °C/min. Reported data are from the second full cycle. The temperature ranged from -100 to 100 °C.

Thermogravimetric analyses were measured under nitrogen with a TGA Q5000 from TA Instruments. About 5-10 mg of each sample were heated at 50 °C/min from 25 to 500 °C.

Gel permeation chromatography (GPC) was performed at 40 °C using a Waters Associates GPCV2000 liquid chromatography system with an internal differential refractive index detector and two Waters Styragel HR-5E columns (10 μm PD, 7.8 mm i.d., 300 mm length) using HPLC grade tetrahydrofuran (THF) as the mobile phase at a flow rate of 1.0 mL/min. Calibration was performed with narrow polydispersity polystyrene standards.

Monomer Preparation

1,5-pentanediol. 1,5-pentanediol was purchased from Acros Organics as a liquid in 98% purity. The monomer was further purified by first stirring it over calcium hydride for 24 hours followed by vacuum distillation. The purified monomer was stored over molecular sieves.

1,6-hexanediol. 1,6-hexanediol was purchased from Acros Organics as a crystalline solid in 97 % purity. The monomer was further purified by recrystallization from ethyl acetate.

1,7-heptanediol. 1,7-pentanediol was purchased from Aldrich as a liquid in 95% purity. The monomer was further purified via the same method as for 1,5-pentanediol above.

1,8-octanediol. 1,8-octanediol was purchased from Acros Organics as a crystalline solid in 99% purity. The

monomer was further purified by recrystallization from ethyl acetate.

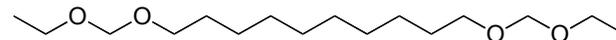
1,9-nonanediol. 1,9-nonanediol was purchased from Acros Organics as a crystalline solid in 99% purity. The monomer was further purified by recrystallization from ethyl acetate.

1,10-decanediol. 1,10-decanediol was purchased from Acros Organics as a crystalline solid in 99% purity. The monomer was further purified by recrystallization from 1,2-dichloroethane.

1,11-undecanediol. 1,11-undecanediol was prepared by utilizing a tandem reduction-hydroboration reaction on methyl 10-undecenoate according to literature methods.¹ The product was purified by recrystallization from 1,2-dichloroethane. Methyl 10-undecenoate was purchased from Aldrich and used as received. ^1H NMR (DMSO-*d*₆): δ ppm 1.24 (s, 14 H), 1.39 (m, 4 H), 3.37 (m, 4 H), 4.31 (br s, 2 H). ^{13}C NMR (DMSO-*d*₆): δ 25.5, 28.97, 29.01, 29.1, 32.6, 60.7.

1,12-dodecanediol. 1,12-dodecanediol was purchased from Aldrich as a crystalline solid in 99% purity. The monomer was further purified by recrystallization from 1,2-dichloroethane.

3,5,16,18-tetraoxaicosane. (decanediol bis-acetal)



A 1 liter round bottom flask was charged with 17.43g (0.1 mol, 1 eq.) of 1,10-decanediol, 208.30g (2 mol, 20 eq.) of diethoxymethane, 0.190g (1 mol%) of *para*-toluenesulfonic acid, and 100 mL of toluene. A distillation head was added to the flask and the mixture was heated for 24 hours to distill out principally the ethanol. When ethanol side product was no longer produced, the distillation head was replaced by a reflux condenser and the mixture was then refluxed for 48 hours. After cooling, the reaction was quenched with 3 mL of triethylamine. Most of the toluene and the excess diethoxymethane were removed by rotary evaporation before placing the mixture on the Schlenk line for further drying over 24 hours under dynamic vacuum. The liquid product was then passed through a basic alumina column to give the product as a colorless oil in 72% yield (21.03 g). ^1H NMR (CDCl₃): δ ppm 1.17 (m, 6 H), 1.29 (m, 12 H), 1.54 (m, 4 H), 3.48 (t, *J*=6.7 Hz, 4 H), 3.55 (q, *J*=7.0 Hz, 4 H), 4.62 (s, 4 H). ^{13}C NMR (CDCl₃): δ ppm 15.1, 26.1, 29.3, 29.4, 29.7, 62.9, 67.7, 94.9.

Polymerizations

Polymerization apparatus. Initially, polymerizations were conducted with a distillation head to facilitate the investigation of volatile polymerization side products. Otherwise, the polymerizations were typically conducted in a round bottom flask, connected to a rotary evaporation bump trap, connected to a vacuum line. With this apparatus molecules of condensation could be collected and visualized in the bump trap, followed by removal of all volatiles—without changing the initial glassware configuration. See below.



General work-up procedure for all polymerizations.

The product was dissolved in a minimal amount of methylene chloride. 1 mL of aqueous 1M NaOH solution was added to the mixture to quench any excess acid. The polymer was crashed out of solution by pouring the mixture into 300 mL of cold methanol. The system was filtered and the polymer was washed with copious amounts of methanol, acetone, and finally ether. The polymer was dried under vacuum overnight.

Polypentylene acetal

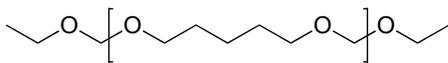


Table S1, Entry 1. A 100 mL round bottom flask was charged with 1.04 g (10 mmol) of 1,5-pentanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 15 mL of xylenes, and 37.55 mL (300 mmol) of diethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 2 hours. Once the time had expired, the temperature was then again raised to 135 °C and stirred for an additional 2 hours. After this step, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for only 1 hour to avoid the loss of the monomer as the cyclic acetal. Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 48% yield (0.55 g). ¹H NMR (CDCl₃): δ ppm 1.44 (m, 2 H), 1.62 (m, 4 H), 3.53 (t, *J*=6.7 Hz, 4 H), 4.66 (s, 2 H). ¹³C NMR (CDCl₃): δ ppm 22.9, 29.5, 67.6, 95.2.

Polyhexylene acetal

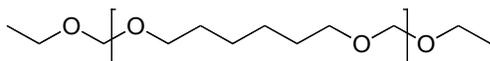


Table S1, Entry 2. A 100 mL round bottom flask was charged with 1.18 g (10 mmol) of 1,6-hexanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 15 mL of xylenes, and 37.55 mL (300 mmol) of diethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 2 hours. Once

the time had expired, the temperature was then again raised to 135 °C and stirred for an additional 2 hours. After this step, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for only 1 hour to avoid the loss of the monomer as the cyclic acetal. Once cool, the aforementioned work-up procedure was applied to give the polymer as white powder in 27% yield (0.35 g). ¹H NMR (CDCl₃): δ ppm 1.38 (dt, *J*=7.4, 3.7 Hz, 4 H), 1.59 (t, *J*=6.5 Hz, 4 H), 3.52 (m, 4 H), 4.66 (m, 2 H). ¹³C NMR (CDCl₃): δ ppm 26.3, 29.9, 67.9, 95.5.

Polyheptylene acetal

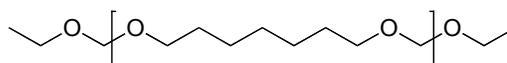


Table S1, Entry 3. A 100 mL round bottom flask was charged with 1.32 g (10 mmol) of 1,7-heptanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 15 mL of xylenes, and 37.55 mL (300 mmol) of diethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 1 hour. This was done to remove the ethanol, a by-product of the first stage of the polymerization. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 12 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 64% yield (0.93 g). ¹H NMR (CDCl₃): δ ppm 1.37 (m, 6 H), 1.57 (m, 4 H), 3.52 (t, *J*=6.5 Hz, 4 H), 4.66 (s, 2 H). ¹³C NMR (CDCl₃): δ ppm 26.2, 29.3, 29.7, 67.8, 95.2.

Polyoctylene acetal

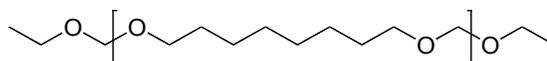


Table S1, Entry 4. A 100 mL round bottom flask was charged with 1.46 g (10 mmol) of 1,8-octanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 15 mL of xylenes, and 37.55 mL (300 mmol) of diethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 1 hour. This was done to remove the ethanol, a by-product of the first stage of the polymerization. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 12 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 79% yield (1.25 g). ¹H NMR (CDCl₃) δ ppm 1.31 (br s, 8 H), 1.56 (m, 4 H), 3.50 (t, *J*=6.5 Hz, 4 H), 4.65 (s, 2 H). ¹³C NMR (CDCl₃) δ ppm 26.2, 29.4, 29.7, 67.8, 95.2.

Polynonylene acetal

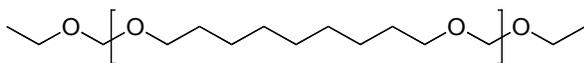


Table S1, Entry 5. A 100 mL round bottom flask was charged with 1.60 g (10 mmol) of 1,9-nonanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 15 mL of xylenes, and 37.55 mL (300 mmol) of diethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 1 hour. This was done to remove the ethanol, a by-product of the first stage of the polymerization. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 12 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 70% yield (1.21 g). ¹H NMR (CDCl₃): δ ppm 1.35 (m, 10 H), 1.57 (q, *J*=6.7 Hz, 4 H), 3.52 (t, *J*=6.6 Hz, 4 H), 4.67 (s, 2 H). ¹³C NMR (CDCl₃): δ ppm 26.2, 29.4, 29.6, 29.8, 67.8, 95.2.

Polydecylene acetal

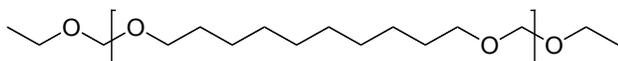


Table S1, Entry 6. A 100 mL round bottom flask was charged with 1.74 g (10 mmol) of 1,10-decanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 15 mL of xylenes, and 37.55 mL (300 mmol) of diethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 1 hour. This was done to remove the ethanol, a by-product of the first stage of the polymerization. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 12 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 82% yield (1.52 g). ¹H NMR (CDCl₃): δ ppm 1.28 (br s, 12 H), 1.56 (m, 4 H), 3.51 (t, *J*=6.7 Hz, 4 H), 4.65 (s, 2 H). ¹³C NMR (CDCl₃): δ ppm 26.2, 29.5, 29.6, 29.8, 67.8, 95.2.

Polydecylene acetal (stepwise procedure from bis-acetal)

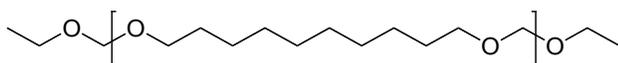


Table S1, Entry 7. A 100 mL round bottom flask was charged with 2.90 g (10 mmol) of 3,5,16,18-tetraoxaicosane (decanediol bis-acetal), and 19 mg (1 mol%) of *para*-toluenesulfonic acid (*p*-TSA). The mixture was stirred under a nitrogen atmosphere for 30 minutes at room temperature before raising the temperature to 125 °C. The mixture was stirred under a nitrogen atmosphere at 125 °C for another 30 minutes before applying vacuum for 2 hours. The vacuum was

introduced at a lower temperature to prevent the evaporative loss of the bis-acetal. The temperature was then raised to 200 °C and the stirring continued for another 10 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 95% yield (1.77 g). The overall yield over the two steps was 68%. ¹H NMR (CDCl₃): δ ppm 1.32 (m, 12 H), 1.55 (m, 4 H), 3.50 (t, *J*=6.6 Hz, 4 H), 4.65 (s, 2 H). ¹³C NMR (CDCl₃): δ ppm 26.2, 29.5, 29.6, 29.7, 67.8, 95.2.

Polyundecylene acetal

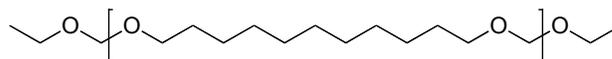


Table S1, Entry 8. A 100 mL round bottom flask was charged with 1.88 g (10 mmol) of 1,11-undecanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), and 37.55 mL (300 mmol) of diethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 1 hour. This was done to remove the ethanol, a by-product of the first stage of the polymerization. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 12 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 86% yield (1.73 g). ¹H NMR (CDCl₃): δ ppm 1.28 (br s, 14 H), 1.57 (m, 4 H), 3.52 (t, *J*=6.6 Hz, 4 H), 4.67 (s, 2 H). ¹³C NMR (CDCl₃): δ ppm 26.3, 29.5, 29.57, 29.60, 29.8, 67.8, 95.2.

Polydodecylene acetal

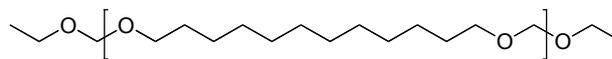


Table S1, Entry 9. A 100 mL round bottom flask was charged with 2.02 g (10 mmol) of 1,12-dodecanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), and 37.55 mL (300 mmol) of diethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 1 hour. This was done to remove the ethanol, a by-product of the first stage of the polymerization. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 12 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 85 % yield (1.82 g). ¹H NMR (CDCl₃): δ ppm 1.29 (m, 16 H), 1.57 (m, 4 H), 3.52 (t, *J*=6.7 Hz, 4 H), 4.67 (s, 2 H). ¹³C NMR (CDCl₃): δ ppm 26.3, 29.5, 29.62, 29.62, 29.8, 67.8, 95.2.

Polydecylene acetal (10.00 g scale)

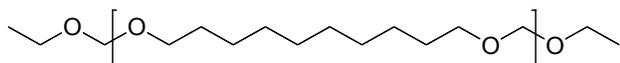


Table S1, Entry 10. A 500 mL round bottom flask equipped with a distillation head was charged with 50.00 g (57.4 mmol, 1 eq) of 1,10-decanediol, 213 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 75.0 mL of xylenes, and 215 mL (1.72 mol, 30 eq) of diethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 1 hour. This was done to remove the ethanol, a by-product of the first stage of the polymerization. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 12 hours and then the distillation head was removed. The system was then placed under vacuum for an additional 6 hours before cooling. Once cool, the reaction mixture was dissolved in 100 mL of dichloromethane and the polymer precipitated out in 500 mL of cold basic methanol. The polymer was then isolated by filtration and washed with copious amounts of acetone and then diethyl ether. After filtration and drying, the polymer was isolated as a white powder in 68.2 % yield (7.28 g). ¹H NMR (CDCl₃): δ ppm 1.30 (m, 12 H), 1.57 (m, 4 H), 3.52 (t, *J*=6.6 Hz, 4 H), 4.67 (s, 2 H) ¹³C NMR (CDCl₃): δ ppm 26.2, 29.5, 29.6, 29.8, 67.8, 95.2.

Polydecylene acetal (50.00 g scale)

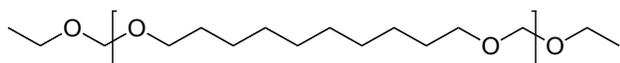


Table S1, Entry 11. A 3-neck 1 L round bottom flask equipped with a distillation head was charged with 50.00 g (287 mmol, 1 eq) of 1,10-decanediol, 1.09 g (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 250 mL of 1,1,2,2-tetrachloroethane, and 500 mL (3.99 mol, 13.9 eq) of diethoxymethane. 1,1,2,2-tetrachloroethane was utilized in this case because the solvent better dissolves the reaction mixture at such concentrations. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 1 hour. This was done to remove the ethanol, a by-product of the first stage of the polymerization. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 12 hours and then the distillation head was removed. The system was then placed under vacuum for an additional 6 hours before cooling. Once cool, the reaction mixture was dissolved in 300 mL of dichloromethane and the polymer precipitated out in 1.5 L of cold basic methanol. The polymer was then isolated by filtration and washed with copious amounts of acetone and then diethyl ether. After filtration

and drying, the polymer was isolated as a white powder in 91% yield (48.65 g). ¹H NMR (CDCl₃): δ ppm 1.33 (m, 12 H), 1.58 (m, 4 H), 3.52 (t, *J*=6.6 Hz, 4 H), 4.67 (s, 2 H). ¹³C NMR (CDCl₃): δ ppm 26.2, 29.5, 29.6, 29.8, 67.8, 95.2.

Polydecylene acetal (iterative exp., 1st iteration)

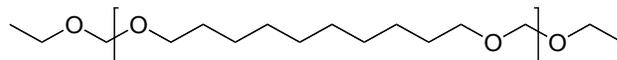


Table S1, Entry 12. A 100 mL pear flask was charged with 2.18 g (12.5 mmol) of 1,10-decanediol, 25 mg (1.1 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 30 mL of toluene, and 20 mL (160 mmol) of diethoxymethane. The flask was then equipped with a distillation head and the mixture was stirred under a nitrogen atmosphere for 30 minutes at 80 °C. The temperature was then raised to 125 °C over 12 hours. By this time, no volatile polymerization by-products were distilling from the reaction. The reaction was placed under dynamic vacuum, still at 125 °C, and left for another 24 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 96% yield (2.23 g). ¹H NMR (CDCl₃): δ ppm 1.27 (m, 12 H), 1.57 (m, 4 H), 3.51 (t, *J*=6.7 Hz, 4 H), 4.66 (s, 2 H). ¹³C NMR (CDCl₃): δ ppm 26.2, 29.4, 29.5, 29.7, 67.8, 95.2.

Polydecylene acetal (iterative exp., 2nd iteration)

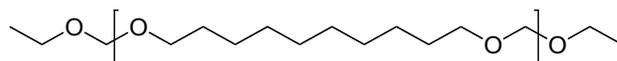


Table S1, Entry 13. A 50 mL round bottom flask was charged with 500 mg sample of polydecylene acetal [*M*_n=7,800; PDI=1.67], 19 mg of *para*-toluenesulfonic acid (*p*-TSA), 18.78 mL (150 mmol) of diethoxymethane, and 10 mL of xylenes. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another hour. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 3 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a fluffy white powder in 70% yield (0.35 g) [*M*_n=29,200; PDI=2.37]. ¹H NMR (CDCl₃): δ ppm 1.33 (m, 12 H), 1.57 (m, 4 H), 3.52 (t, *J*=6.7 Hz, 4 H), 4.67 (s, 2 H). ¹³C NMR (CDCl₃): δ ppm 26.2, 29.5, 29.6, 29.8, 67.8, 95.2.

Polydodecylene acetal (iterative exp., 1st iteration)

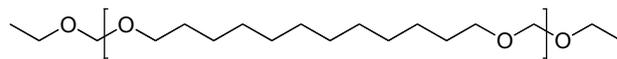


Table S1, Entry 14. A 100 mL round bottom flask was charged with 2.02 g (10 mmol) of 1,12-dodecanediol, 1.9 mg (0.1 mol%) of *para*-toluenesulfonic acid (*p*-TSA), and 37.55 mL (300 mmol) of diethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 1 hour. This was done to

remove the ethanol, a by-product of the first stage of the polymerization. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 12 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 91% yield (1.96 g) [$M_n=8,900$, PDI=1.70]. ^1H NMR (CDCl_3): δ ppm 1.30 (m, 16 H), 1.58 (m, 4 H), 3.52 (t, $J=6.7$ Hz, 4 H), 4.67 (s, 2 H). ^{13}C NMR (CDCl_3): δ ppm 26.3, 29.5, 29.61, 29.61, 29.8, 67.8, 95.2.

Polydodecylene acetal (iterative exp., 2nd iteration)

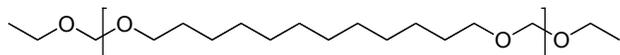


Table S1, Entry 15. A 50 mL round bottom flask was charged with 500 mg of polydodecylene acetal [$M_n=8,900$, PDI=1.70], 19 mg of *para*-toluenesulfonic acid (*p*-TSA), 18.78 mL (150 mmol) of diethoxymethane, and 10 mL of xylenes. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another hour. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 3 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a fluffy white powder in 74% yield (0.37 g) [$M_n=27,600$, PDI=2.26]. ^1H NMR (CDCl_3): δ ppm 1.33 (m, 16 H), 1.58 (m, 4 H), 3.52 (t, $J=6.7$ Hz, 4 H), 4.67 (s, 2 H). ^{13}C NMR (CDCl_3): δ ppm 26.3, 29.5, 29.62, 29.62, 29.8, 67.8, 95.2.

Polydecylene acetal (from dimethoxymethane)

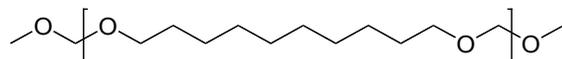


Table S1, Entry 16. A 100 mL round bottom flask was charged with 1.74 g (10 mmol) of 1,10-decanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 15 mL of xylenes, and 26.5 mL (300 mmol) of dimethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 1 hour. This was done to remove the methanol, a by-product of the first stage of the polymerization. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 12 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 76% yield (1.41 g). ^1H NMR (CDCl_3): δ ppm 1.33 (m, 12 H), 1.57 (m, 4 H), 3.52 (t, $J=6.7$ Hz, 4 H), 4.67 (s, 2 H). ^{13}C NMR (CDCl_3): δ ppm 26.3, 29.5, 29.6, 29.8, 67.8, 95.2.

Polydodecylene acetal (from dimethoxymethane)

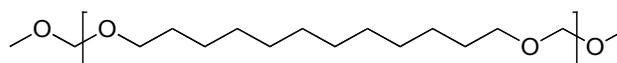


Table S1, Entry 17. A 100 mL round bottom flask was charged with 2.02 g (10 mmol) of 1,12-dodecanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 15 mL of xylenes, and 26.5 mL (300 mmol) of dimethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 1 hour. This was done to remove the methanol, a by-product of the first stage of the polymerization. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 12 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 76% yield (1.63 g). ^1H NMR (CDCl_3): δ ppm 1.33 (m, 16 H), 1.58 (m, 4 H), 3.52 (t, $J=6.7$ Hz, 4 H), 4.67 (s, 2 H). ^{13}C NMR (CDCl_3): δ ppm 26.3, 29.5, 29.62, 29.62, 29.8, 67.8, 95.2.

Polydecylene acetal (diethoxymethane:diol is 2:1)

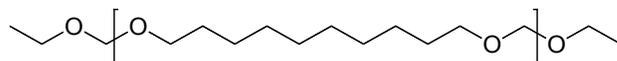


Table S1, Entry 18. A 100 mL round bottom flask was charged with 1.74 g (10 mmol) of 1,10-decanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 15 mL of xylenes, and 2.50 mL (20 mmol) of diethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 1 hour. This was done to remove the methanol, a by-product of the first stage of the polymerization. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 12 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 82% yield (1.53 g). ^1H NMR (CDCl_3): δ ppm 1.33 (m, 12 H), 1.58 (m, 4 H), 3.52 (t, $J=6.7$ Hz, 4 H), 4.67 (s, 2 H). ^{13}C NMR (CDCl_3): δ ppm 26.2, 29.5, 29.6, 29.8, 67.8, 95.2.

Polydecylene acetal (dimethoxymethane:diol is 2:1)

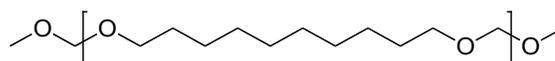


Table S1, Entry 19. A 100 mL round bottom flask was charged with 1.74 g (10 mmol) of 1,10-decanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 15 mL of xylenes, and 1.77 mL (20 mmol) of dimethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 1 hour. This was done to remove the methanol, a by-product of the first

stage of the polymerization. Once the time had expired, the temperature was then again raised to 200 °C over a period of 2 hours still under a nitrogen atmosphere. After this time interval was over, the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 12 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 49% yield (0.91 g). ¹H NMR (CDCl₃): δ ppm 1.34 (m, 12 H), 1.58 (m, 4 H), 3.52 (t, *J*=6.7 Hz, 4 H), 4.67 (s, 2 H). ¹³C NMR (CDCl₃): δ ppm 26.2, 29.5, 29.6, 29.8, 67.8, 95.2.

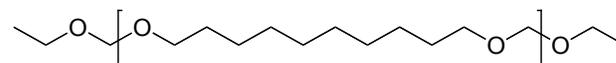
Attempted polymerization with ethylene glycol. A 100 mL round bottom flask was charged with 0.62 g (10 mmol) of ethylene glycol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 15 mL of xylenes, and 37.55 mL (300 mmol) of diethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 2 hours. Once the time had expired, the temperature was then again raised to 135 °C and stirred for an additional 2 hours. After this step, the system was placed under dynamic vacuum. The system was kept under vacuum for only 1 hour, at the end of which nothing remained in the reaction flask.

Attempted polymerization with 1,3-propanediol. A 100 mL round bottom flask was charged with 0.76 g (10 mmol) of 1,3-propanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 15 mL of xylenes, and 37.55 mL (300 mmol) of diethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 2 hours. Once the time had expired, the temperature was then again raised to 135 °C and stirred for an additional 2 hours. After this step, the system was placed under dynamic vacuum. The system was kept under vacuum for only 1 hour, at the end of which nothing remained in the reaction flask.

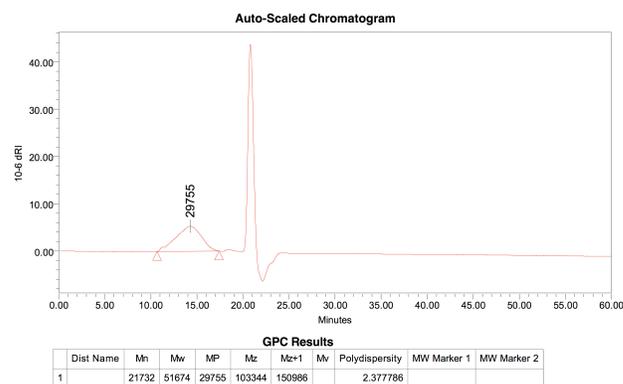
Attempted polymerization with 1,4-butanediol. A 100 mL round bottom flask was charged with 0.90 g (10 mmol) of 1,4-butanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 15 mL of xylenes, and 37.55 mL (300 mmol) of diethoxymethane. The mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 2 hours. Once the time had expired, the temperature was then again raised to 135 °C and stirred for an additional 2 hours. After this step, the system was placed under dynamic vacuum. The system was kept under vacuum for only 1 hour, at the end of which nothing remained in the reaction flask.

Distillate Analysis

Analysis of One-Pot Polymerization Distillate



A 100 mL round bottom flask was charged with 1.74 g (10 mmol) of 1,10-decanediol, 38 mg (2 mol%) of *para*-toluenesulfonic acid (*p*-TSA), 15 mL of xylenes, and 37.55 mL (300 mmol) of diethoxymethane. The flask was then fitted with a distillation head and the mixture was stirred under a nitrogen atmosphere for 1 hour at 80 °C. The temperature was then raised to 115 °C and the stirring continued for another 1 hour. Under these conditions ethanol, the main by-product of the first stage of the polymerization, and diethoxymethane distilled out of the reaction mixture. The presence of ethanol in this first fraction was confirmed by NMR analysis (Figures S1–S2). Once the time had expired, the temperature was then raised to 135 °C and held at said temperature for another hour while a second distillation fraction was collected. This second fraction is clearly rich in diethoxymethane with some trace amounts of xylenes (Figures S3–S4). The diethoxymethane could easily be purified by a second distillation and reused in a subsequent polymerization. The temperature was raised once more to 200 °C and held at that temperature for 1 hour while a third distillation fraction was collected (Figures S5–S6). This fraction was much richer in xylenes but it did contain a significant amount of diethoxymethane. After an hour had expired, the system was placed under vacuum while collection of the fourth fraction was underway. The collection flask for the fourth fraction was cooled with liquid nitrogen to stop the distillate from evaporating under low pressures. Once no more of the fraction was distilling out, the collection flask was replaced with an empty flask and the reaction continued. The system was kept under vacuum for a total of 12 hours before cooling. Analysis of the final fraction indicated that the distillate contained only trace amounts of diethoxymethane and copious amounts of xylenes (Figures S7–S8). Once cool, the aforementioned work-up procedure was applied to give the polymer as a white powder in 75% yield (1.39 g). ¹H NMR (CDCl₃): δ ppm 1.33 (m, 12 H), 1.58 (m, 4 H), 3.52 (t, *J*=6.7 Hz, 4 H), 4.67 (s, 2 H). ¹³C NMR (CDCl₃): δ ppm 26.2, 29.5, 29.6, 29.8, 67.8, 95.2. (*M*_w = 51,674 g/mol; *M*_n = 21,732 g/mol; PDI = 2.38)



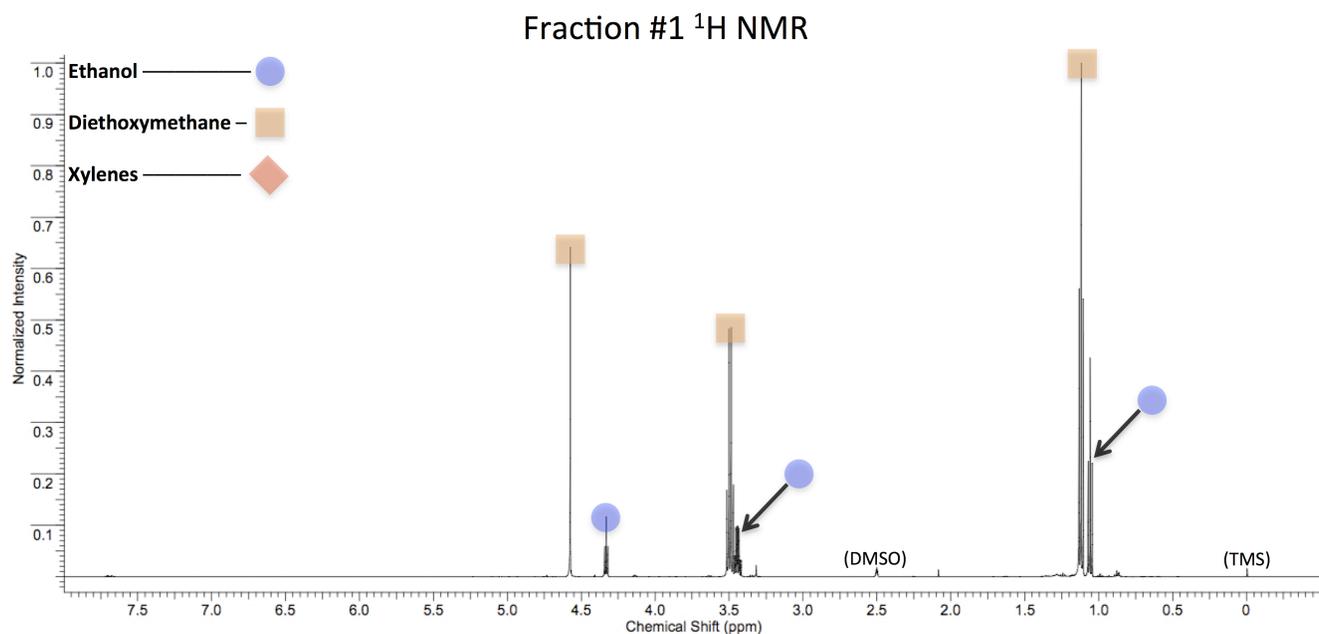


Figure S1. ^1H NMR of the first collected distillation fraction.

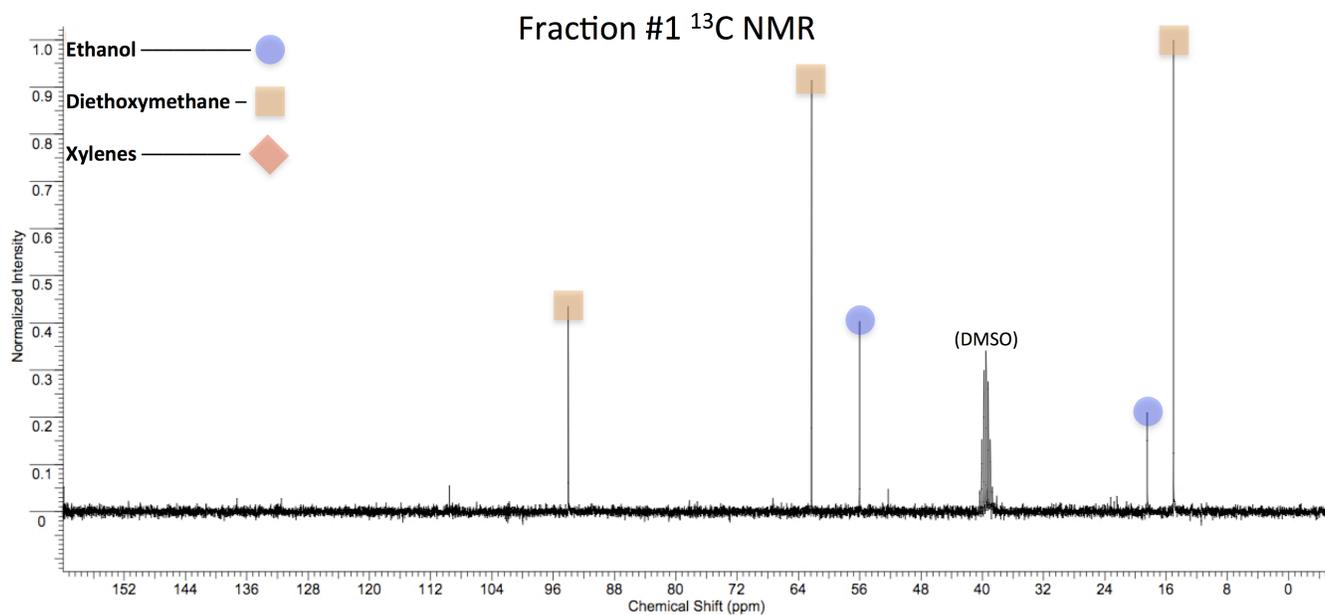


Figure S2. ^{13}C NMR of the first collected distillation fraction.

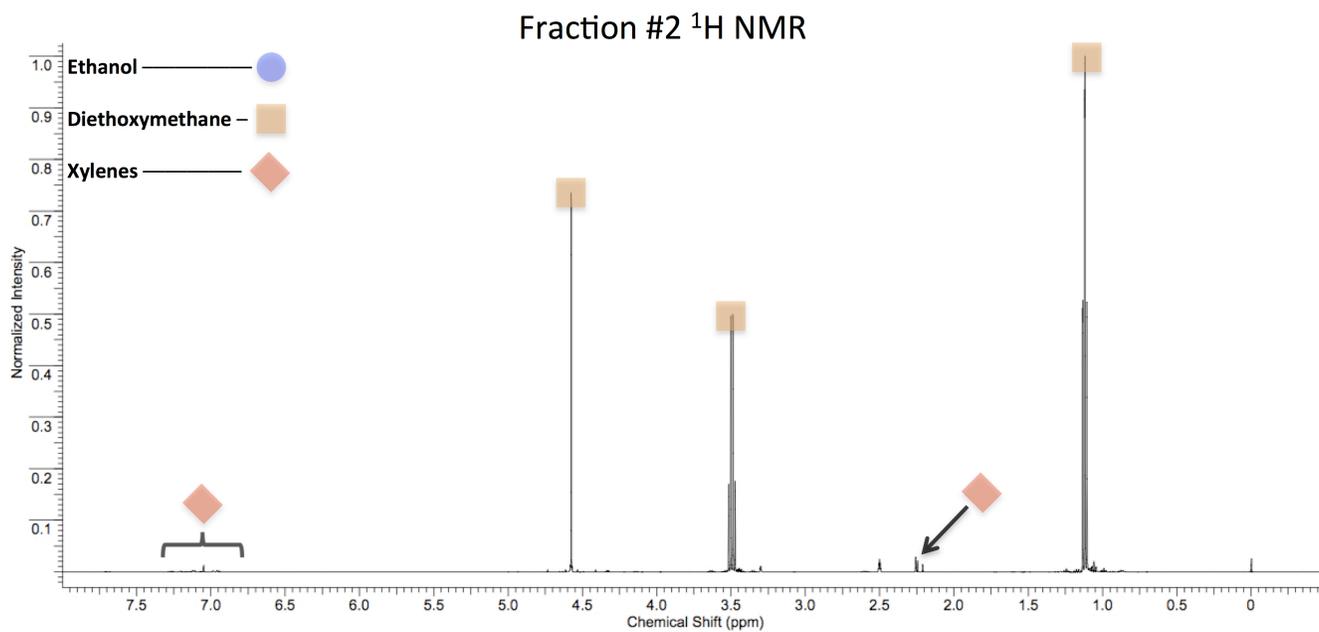


Figure S3. ^1H NMR of the second collected distillation fraction.

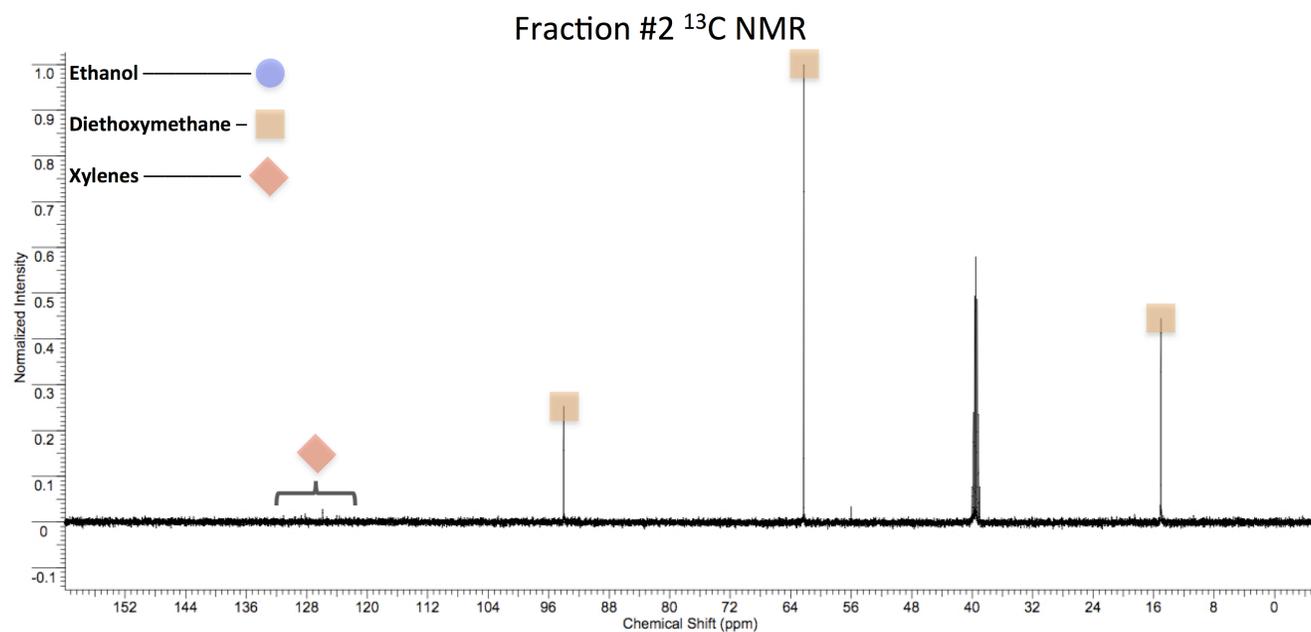


Figure S4. ^{13}C NMR of the second collected distillation fraction.

Fraction #3 ^1H NMR

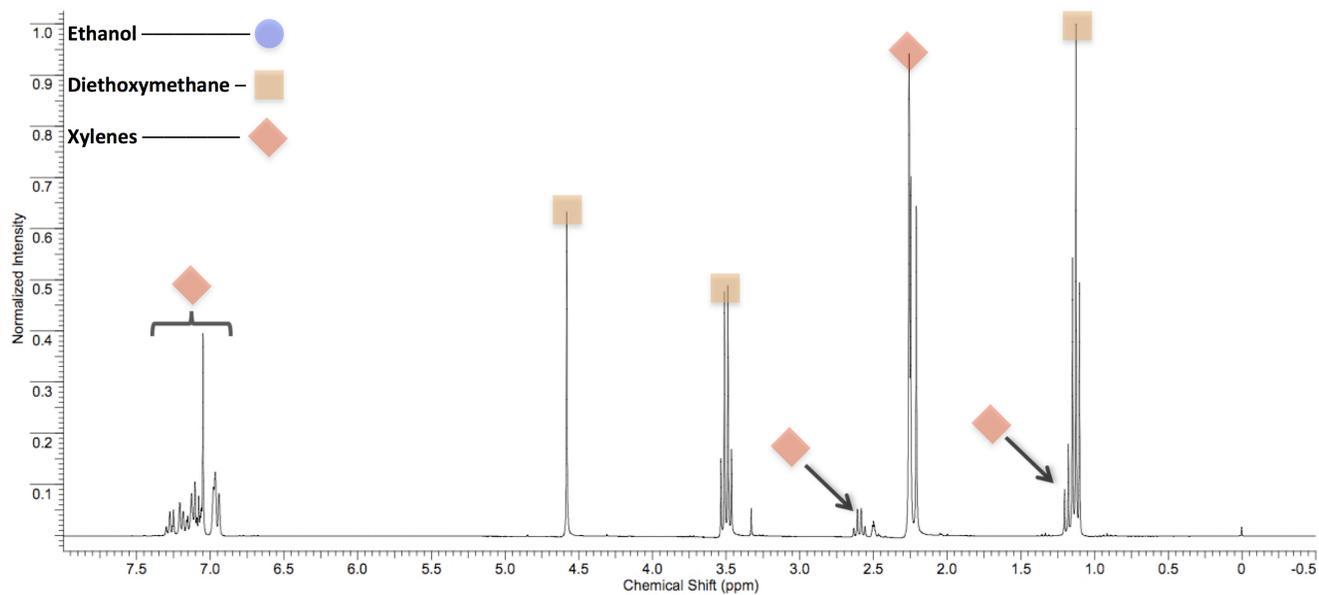


Figure S5. ^1H NMR of the third collected distillation fraction.

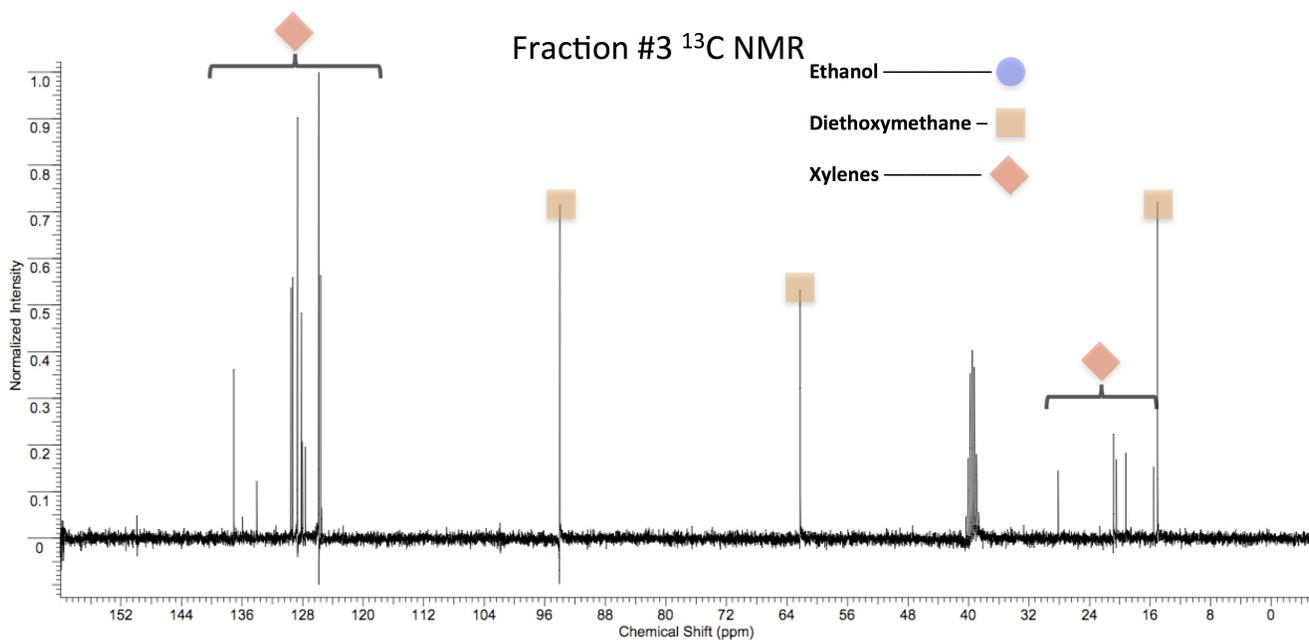


Figure S6. ^{13}C NMR of the third collected distillation fraction.

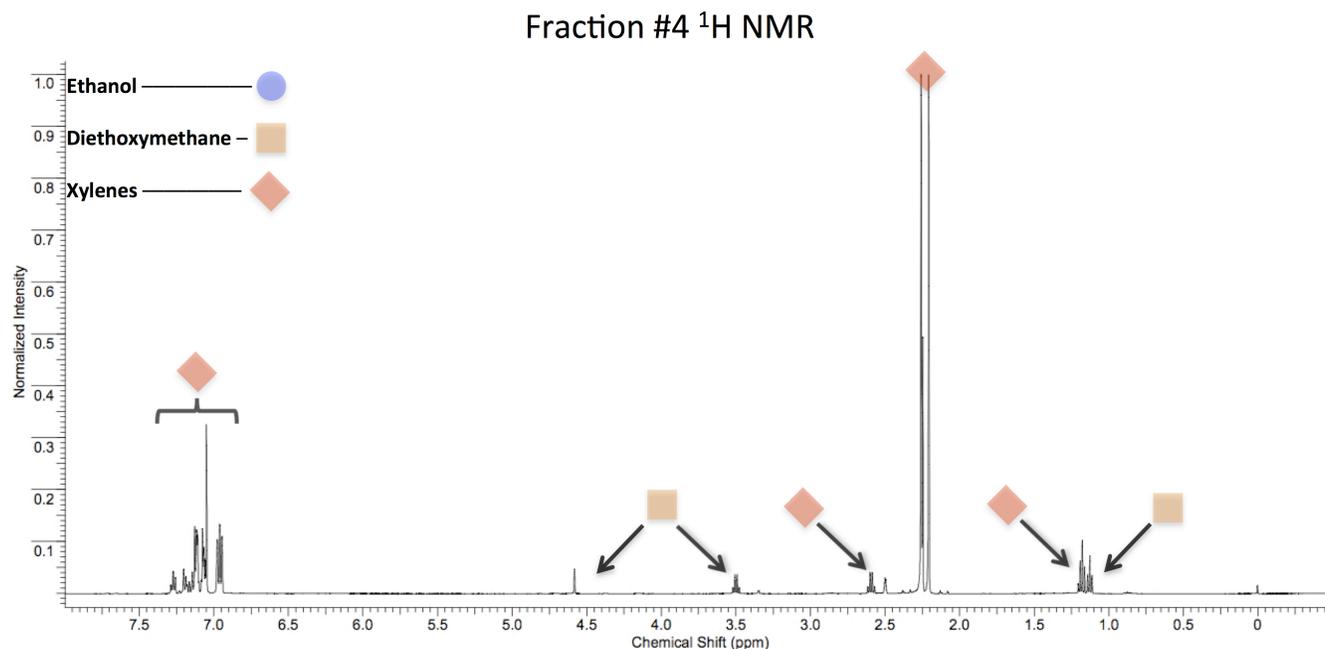


Figure S7. ^1H NMR of the fourth collected distillation fraction.

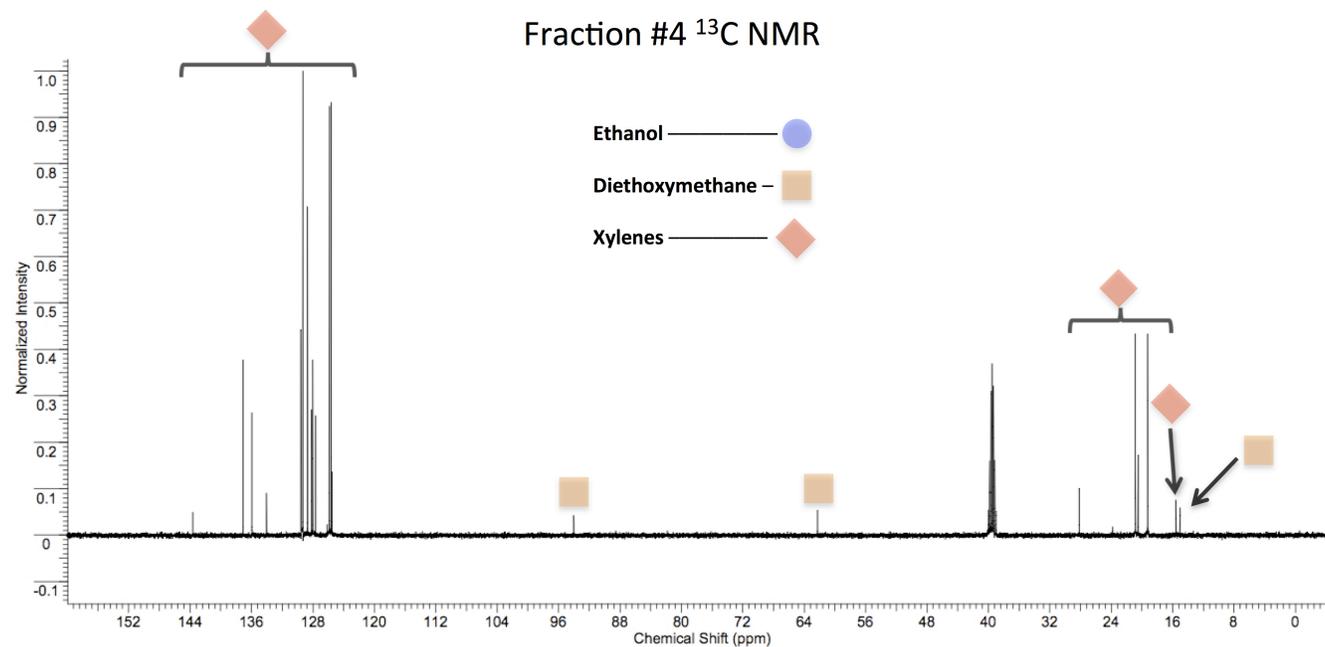


Figure S8. ^{13}C NMR of the fourth collected distillation fraction.

Degradation Studies

The degradation of three polymers was tested. The polymers included polydecylene acetal (PDA), poly-L-lactide (PLLA), and a sample of polylactide from NatureWorks (PLA-600).

PDA Sample Preparation. The preparation of PDA (polydecylene acetal) is detailed in the previous section (Table S1, entry 6).

PLLA Sample Preparation. In a glovebox, a 250 mL round bottom flask was charged with 14.4 g (100 mmol)

of L-lactide, 0.203 g (0.5 mol%) of stannous octoate, 54 mg (0.5 mol%) of benzyl alcohol, and 150 mL of toluene. The mixture was stirred under a nitrogen atmosphere at 100 °C for 24 hours. Once the time interval had expired, the reaction was cooled and the volume reduced by rotary evaporation. The crude mixture was dissolved in a minimal amount of methylene chloride before precipitation in 300 mL of acidic methanol. The precipitate was collected by filtration and dried under vacuum to yield the product in 90% yield.

PLA-600 Sample Preparation. A commercial PLA cup from NatureWorks was dissolved in methylene chloride and the polymer was precipitated in cold methanol. The precipitate was collected by filtration and dried under vacuum to yield the PLA-600 as a white powder.

Degradation Experiment. Solution phase degradation studies were carried out by first dissolving 250 mg of the respective polymer in 100 mL of tetrahydrofuran in a 200 mL airtight jar. 0.5 mL of water and 0.1 mL of sulfuric

acid were then added to each of the jars, which were then placed on an orbital shaker and shaken continuously. 5 mL aliquots were taken from the jars at regular intervals. Each aliquot was worked up by passing the liquid through a basic alumina column. Solvent was then removed from the filtrate by rotary evaporation and the residue tested by gel permeation chromatography. Table S3 contains the GPC data obtained for the three polymers as a function of time.

Summary of Polymerization Data

Table S1. Polymerization results and characterization of polyalkylene acetals.^a

entry	reference	diol	polyalkylene acetal	yield (%)	M_w^b	M_n^b	PDI ^b	T_m (°C)
1 ^c	AP2-85-1			48	13,185	9,710	1.36	38.0
2 ^c	AP2-80-1			27	10,862	8,824	1.23	27.8
3	AP2-77-1			64	62,626	25,822	2.43	46.4
4	AP2-74-1			79	72,344	38,001	1.90	46.5
5	AP2-59-1			70	76,623	38,452	1.99	54.7
6	AP2-65-1			82	62,772	30,531	2.06	58.9
7 ^d	AP2-39-1			68 ^d	40,234	21,956	1.83	59.0
8	AP2-87-1			86	51,426	20,703	2.48	57.2
9	AP2-63-1			85	70,844	37,129	1.91	64.2
10 ^e	AP1-136-1			68	68,041	30,785	2.21	58.2
11 ^f	AP2-148-1			91	60,602	24,569	2.47	57.8
12 ^g	AP1-108-1			96	13,030	7,814	1.67	58.4
13 ^h	AP2-82-1	"12"		70	69,200	29,185	2.37	58.5
14 ^g	AP2-62-1			91	15,241	8,940	1.70	62.9
15 ^h	AP2-84-1	"14"		74	62,537	27,616	2.26	63.8
16 ⁱ	AP2-101-1			76	71,867	35,051	2.05	58.9
17 ⁱ	AP2-102-1			76	78,452	38,697	2.03	64.2
18 ^j	AP2-104-1			82	70,281	32,674	2.15	58.6
19 ^k	AP2-103-1			49	51,530	17,908	2.88	56.5

^a Diethoxymethane: diol = 30:1; 2 mol% *p*-TSA; gradual temperature ramp to 200 °C over 5 h; then dynamic vacuum at 200 °C for 12 h. ^b M_n (g/mol) and polydispersity index (PDI) obtained by GPC in THF at 40 °C with respect to polystyrene standards. ^cVacuum stage of the reaction was performed at 135 °C for only 1 h to limit monomer loss. ^dTwo-step polymerization via isolated bis-acetal; 1 mol% *p*-TSA; yield over two steps. ^eDistillation head employed; 10.0 g of diol; vacuum step performed for 18 h. ^fDistillation head employed; 50.0 g of diol; 1,1,2,2-tetrachloroethane as solvent; diethoxymethane: diol = 13.9:1; vacuum step performed for 18 h. ^gFirst iteration. ^hSecond iteration. ⁱDimethoxymethane: diol = 30:1. ^jDiethoxymethane: diol = 2:1. ^kDimethoxymethane: diol = 2:1.

Table S2. Differential Scanning Calorimetry (DSC)^a and Thermogravimetric Analysis (TGA) data for polyalkylene acetals from Table S1, entries 1–17.

entry	T_m (°C)	ΔH melt (J/g)	T_c (°C)	ΔH cryst (J/g)	T 50% decomp. (°C) ^b
1	38.0	84.1	13.9	82.2	428
2	27.8	85.0	-2.3	63.2	423
3	46.4	73.8	21.2	68.1	423
4	46.5	56.5	26.0	63.9	431
5	54.7	66.2	33.8	74.6	432
6	58.9	74.3	38.0	77.3	405
7	59.0	56.6	34.9	80.8	434
8	57.2	77.1	40.9	72.3	416
9	64.2	105.1	46.1	56.3	431
10	58.2	87.2	36.1	90.9	412
11	57.8	81.4	37.8	86.8	392
12	58.4	125.6	36.2	101.5	400
13	58.5	75.0	34.5	76.5	433
14	62.9	91.5	51.1	96.9	415
15	63.8	84.8	50.3	77.1	424
16	58.9	71.2	37.0	76.0	312
17	64.2	98.9	48.7	61.4	418
18	58.6	78.0	37.0	80.0	411
19	56.5	73.8	38.0	75.0	429

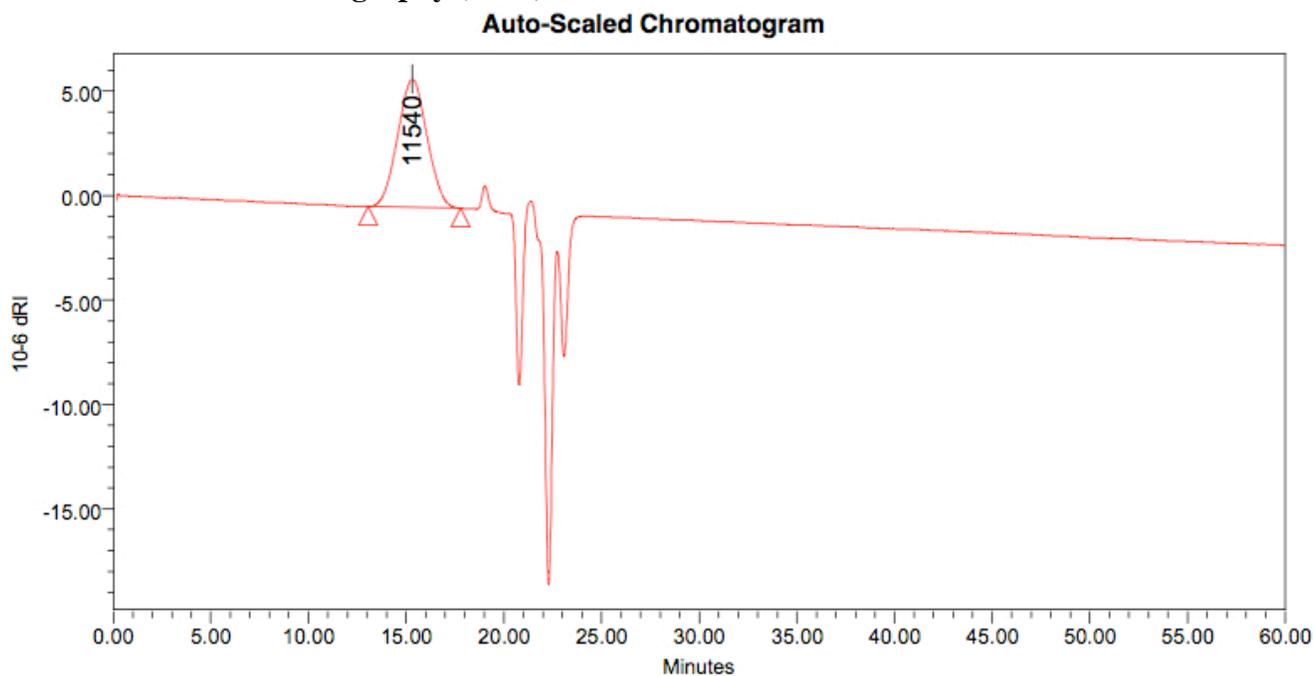
^aDSC Thermal scans conducted from -100 to 100 °C at 10 °C/min. Reported data are from the second full cycle. Crystallization was observed on the cooling scan. ^bThe temperature at which 50% mass loss is observed. TGA was performed under nitrogen.

Table S3. Gel Permeation Chromatography (GPC) data from the degradation studies.^a

aliquot #	time (hours)	polydecylene acetal (PDA)		poly L-lactide (PLLA)		NatureWorks PLA-600	
		M_n	$M_n/M_n(\text{init.})$	M_n	$M_n/M_n(\text{init.})$	M_n	$M_n/M_n(\text{init.})$
0	0	30531	100	38014	100	95752	100
1	3	30061	98	37183	98	93198	97
2	9	27067	89	36524	96	84863	89
3	15	25729	84	35821	94	77666	81
4	21	24989	82	33453	88	71660	75
5	27	22990	75	31359	82	69000	72
6	39	20416	67	30516	80	56067	59
7	51	18638	61	29461	78	47171	49

^a250 mg polymer, 100 mL tetrahydrofuran, 0.5 mL water, and 0.1 mL sulfuric acid. GPC data obtained from aliquots.

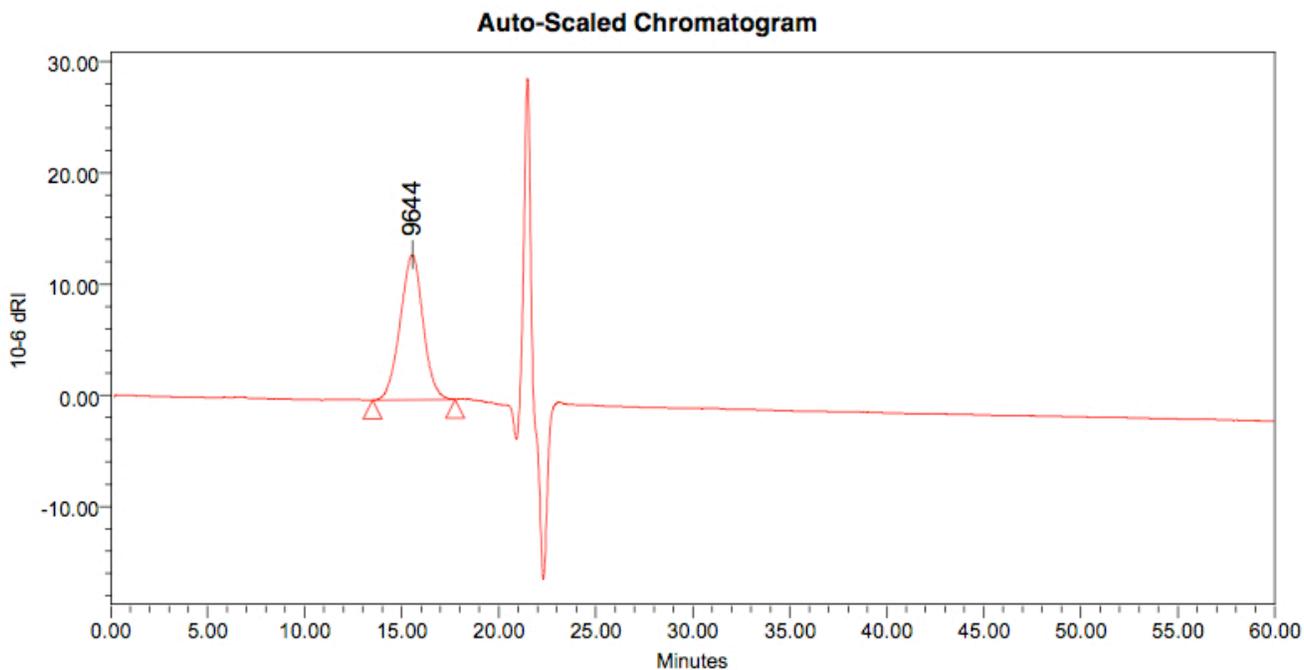
Gel Permeation Chromatography (GPC) Data



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	9710	13185	11540	17524	22591		1.357969		

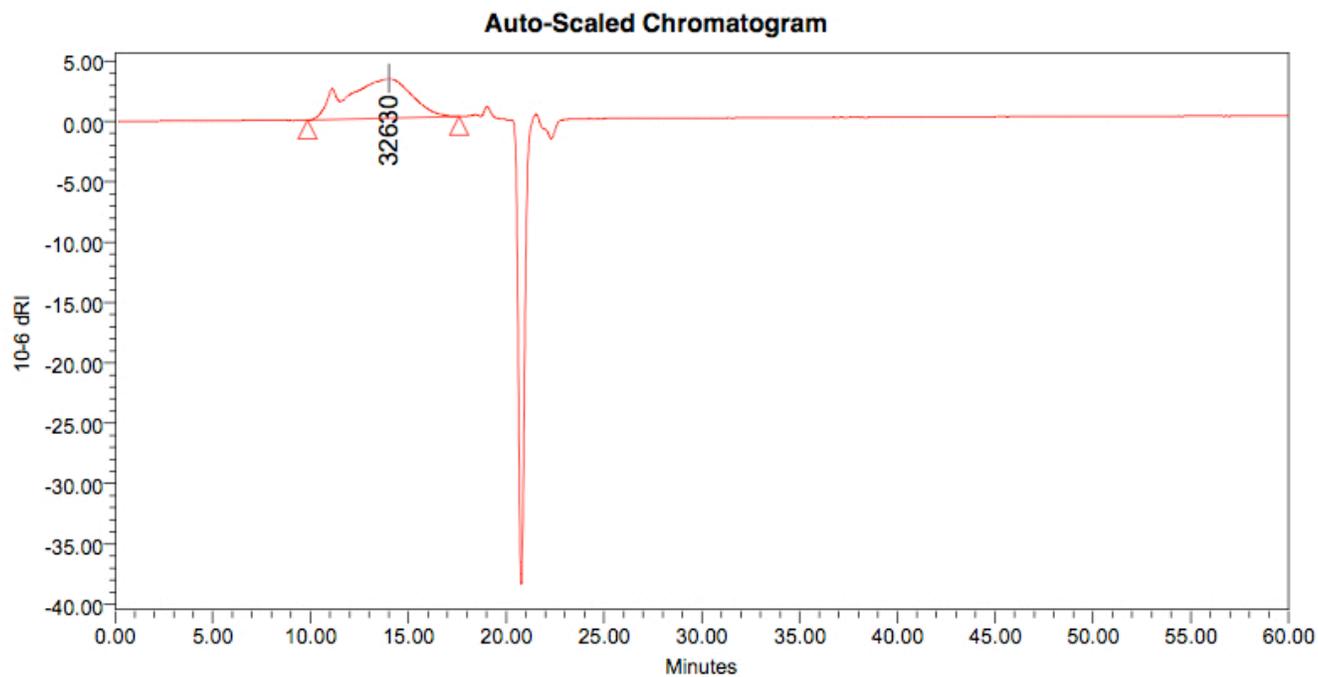
Figure S9. GPC Chromatogram of poly(pentylene acetal) (Table S1, entry 1).



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	8824	10862	9644	13245	16004		1.230964		

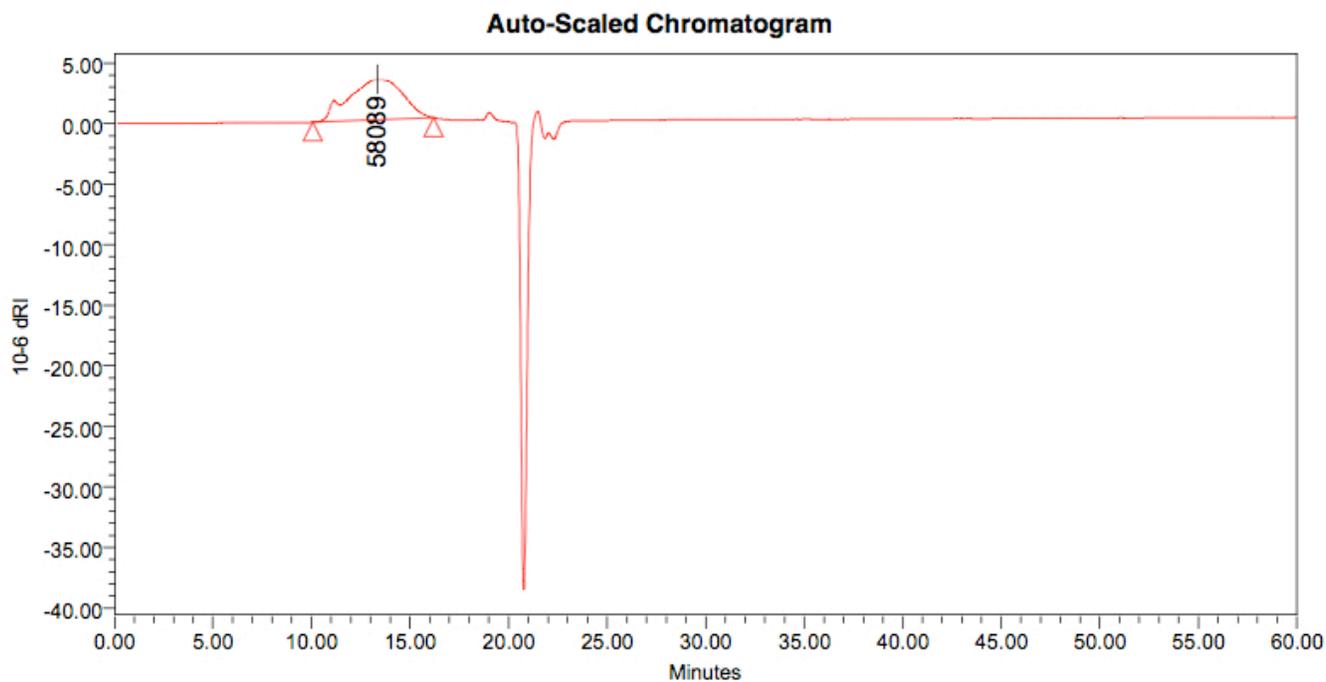
Figure S10. GPC Chromatogram of poly(hexylene acetal) (Table S1, entry 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		25822	62626	32630	117588	161298		2.425305		

Figure S11. GPC Chromatogram of polyheptylene acetal (Table S1, entry 3).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		38001	72344	58089	119349	159016		1.903750		

Figure S12. GPC Chromatogram of polyoctylene acetal (Table S1, entry 4).

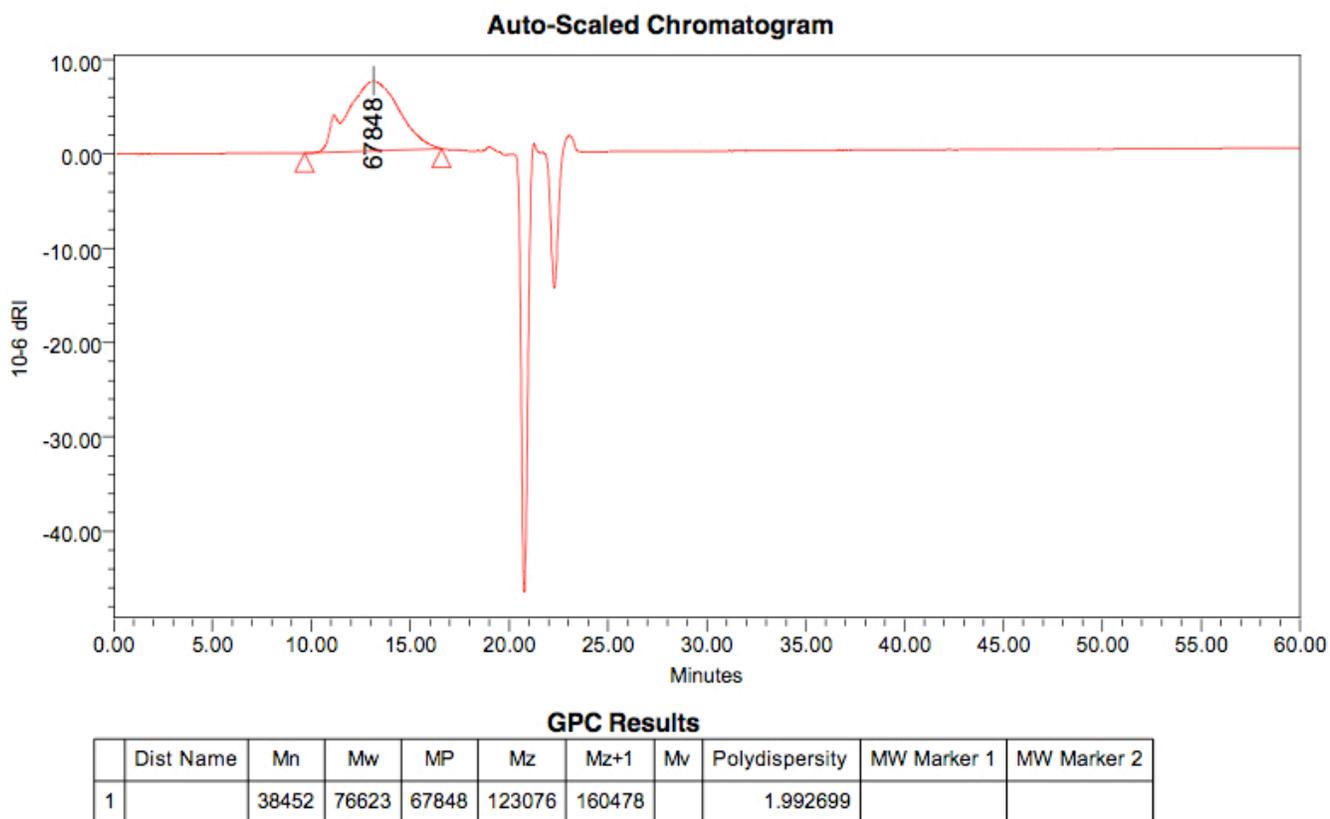


Figure S13. GPC Chromatogram of polynonylene acetal (Table S1, entry 5).

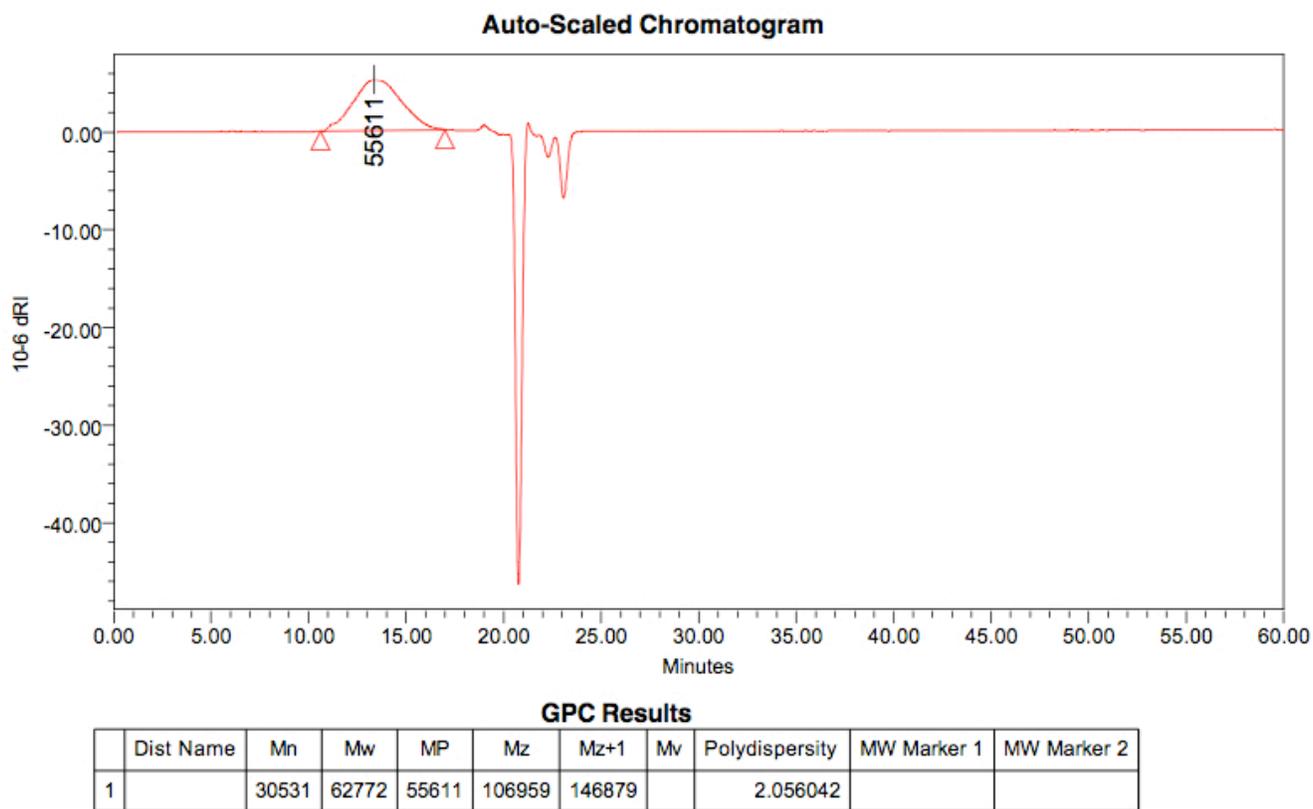


Figure S14. GPC Chromatogram of polydecylene acetal (Table S1, entry 6).

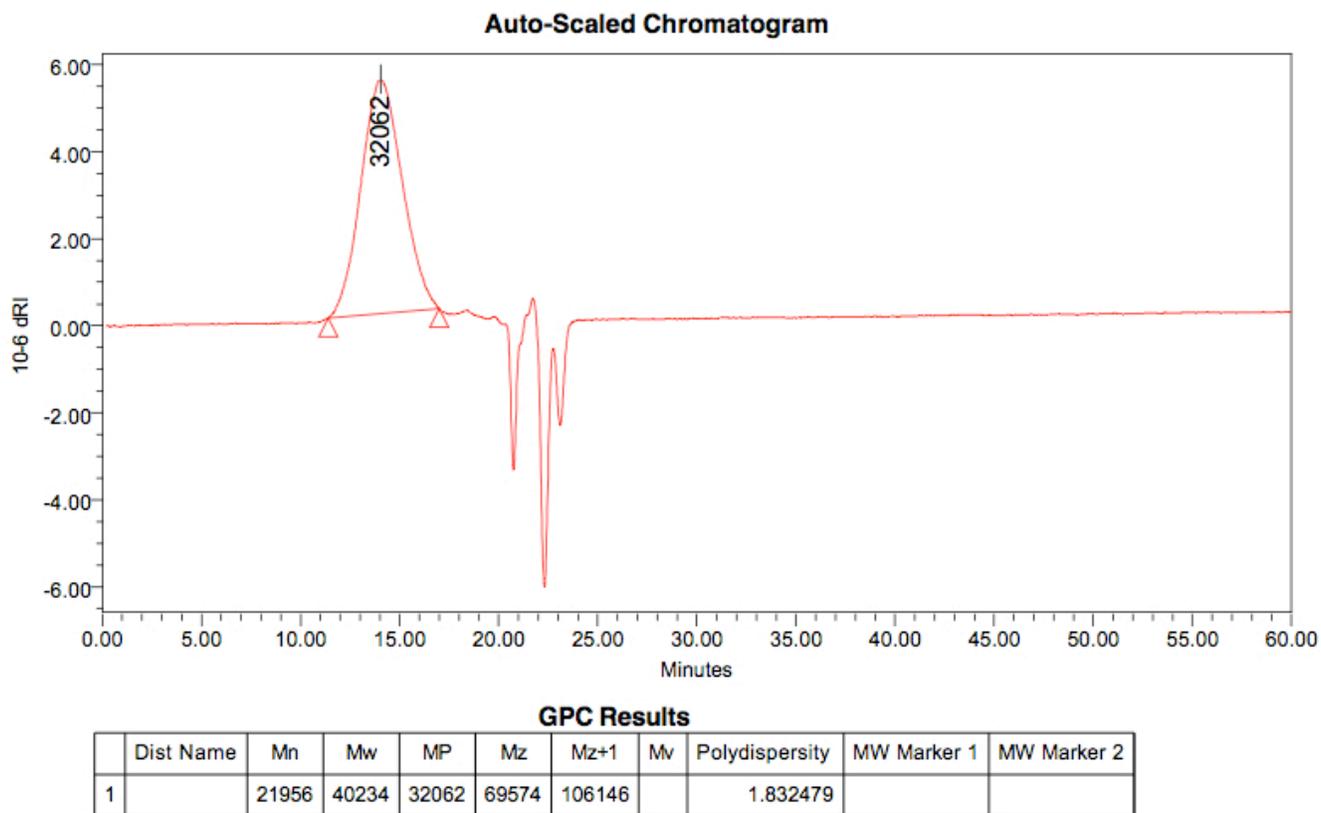


Figure S15. GPC Chromatogram of polydecylene acetal, *from the two-pot synthesis* (Table S1, entry 7).

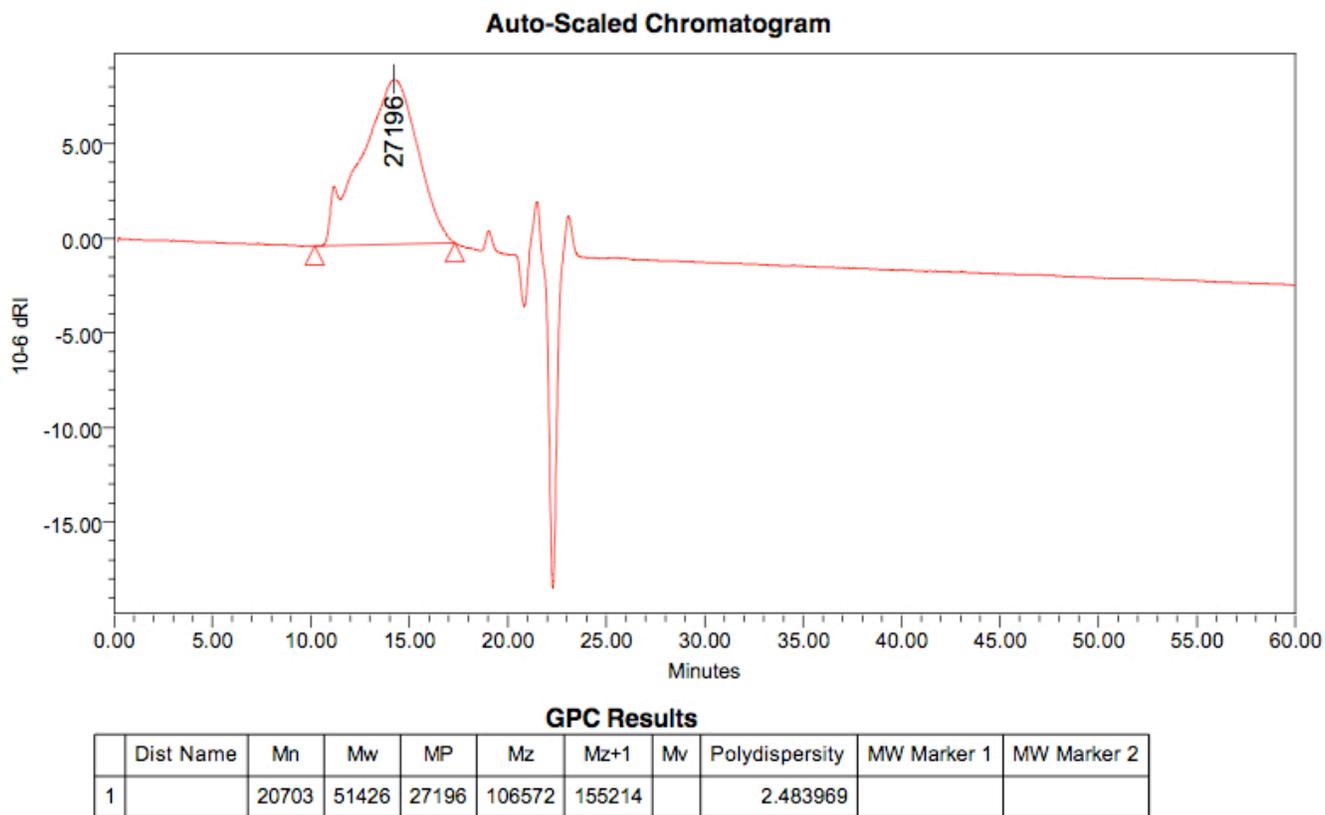
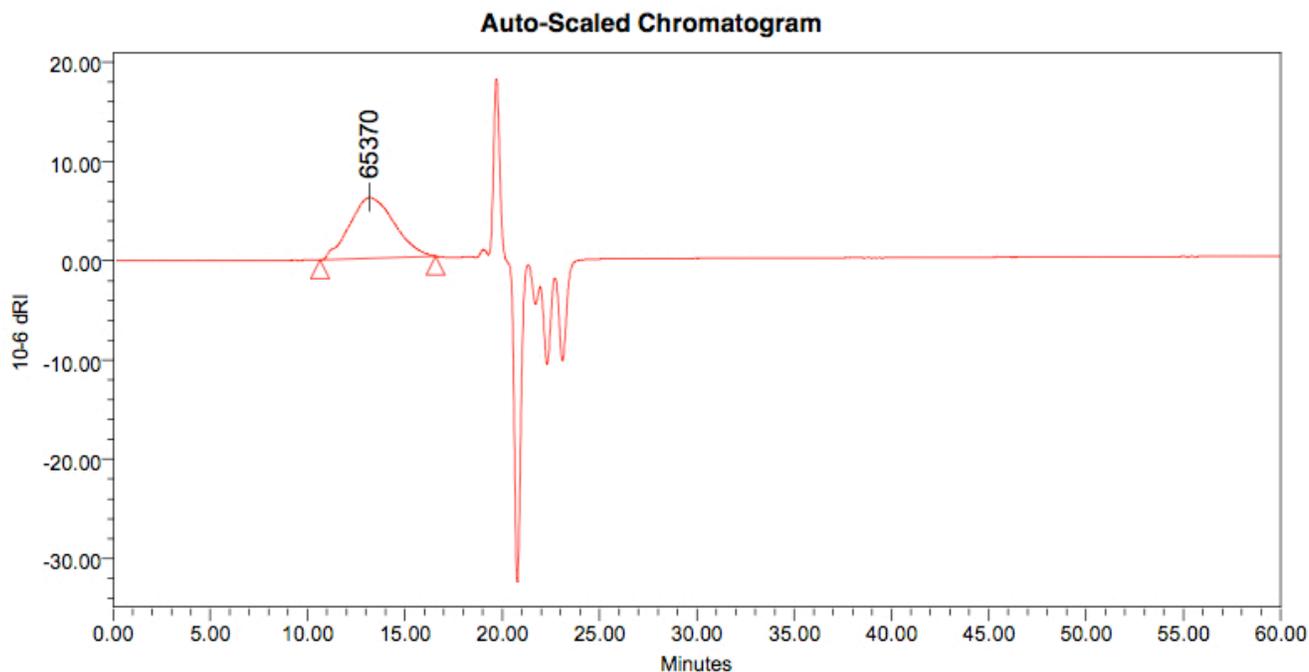


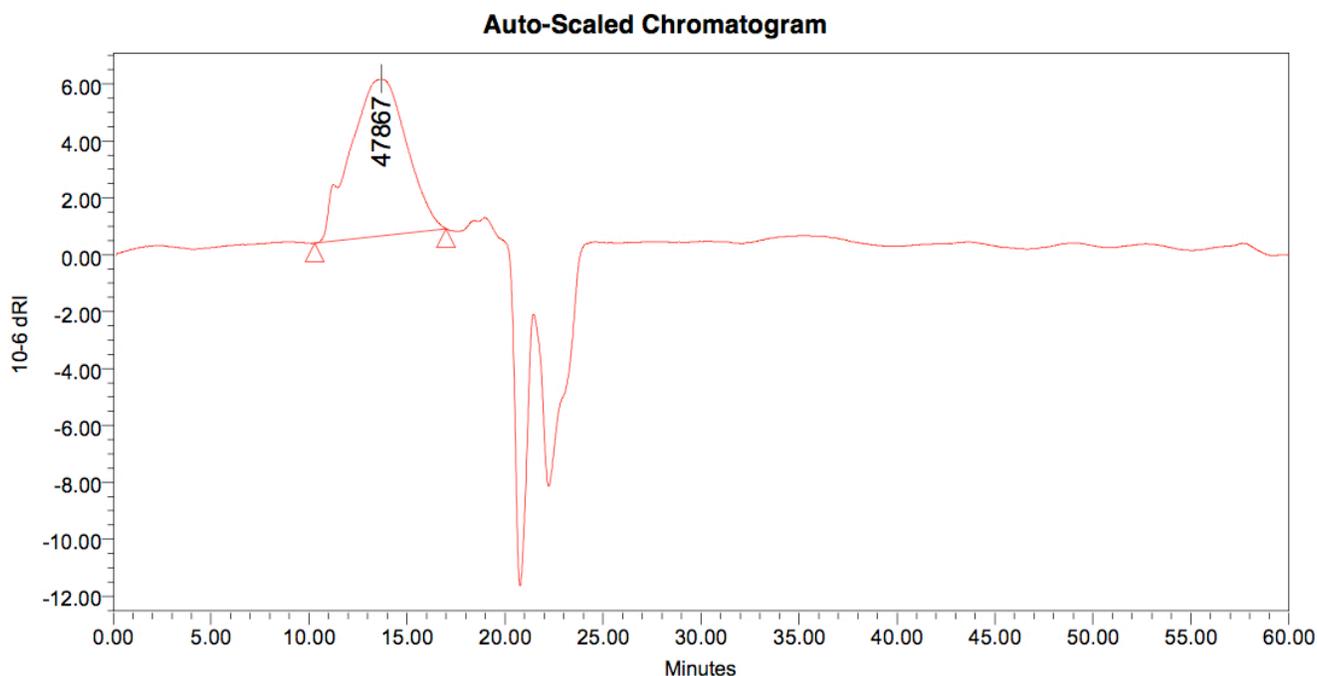
Figure S16. GPC Chromatogram of polyundecylene acetal (Table S1, entry 8).



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	37129	70844	65370	113185	150317		1.908081		

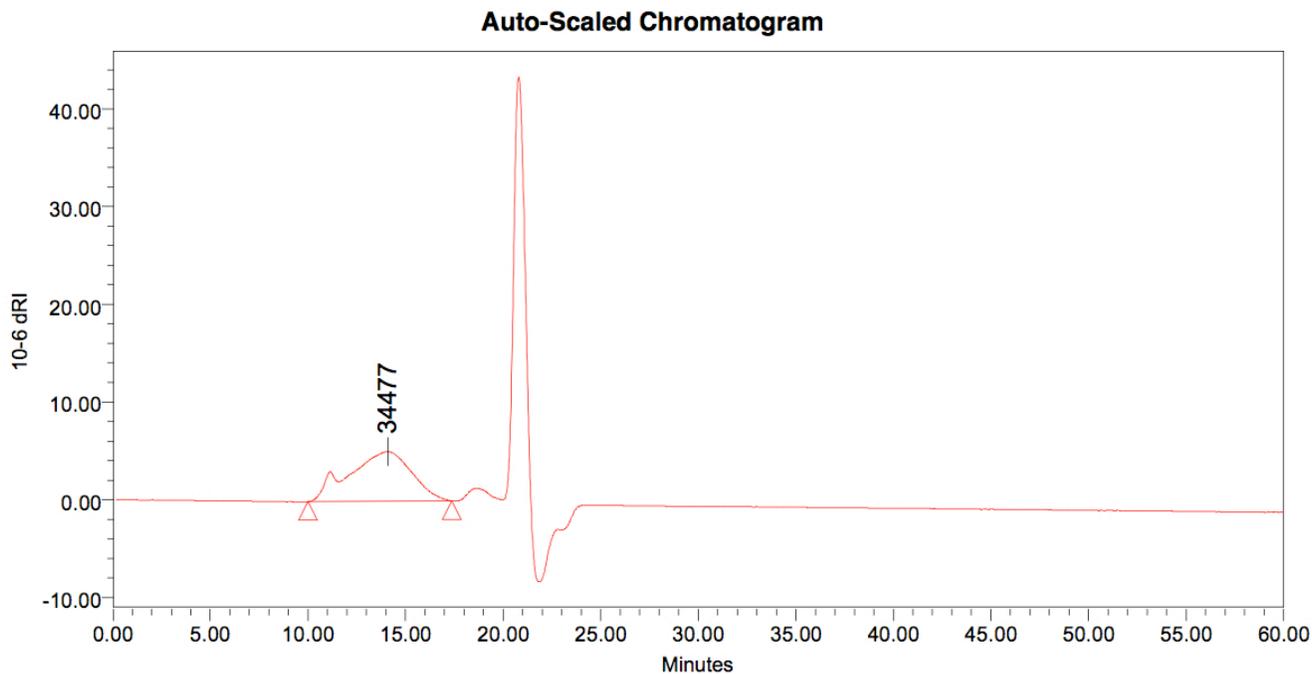
Figure S17. GPC Chromatogram of polydodecylene acetal (Table S1, entry 9).



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	30785	68041	47867	118654	160087		2.210191		

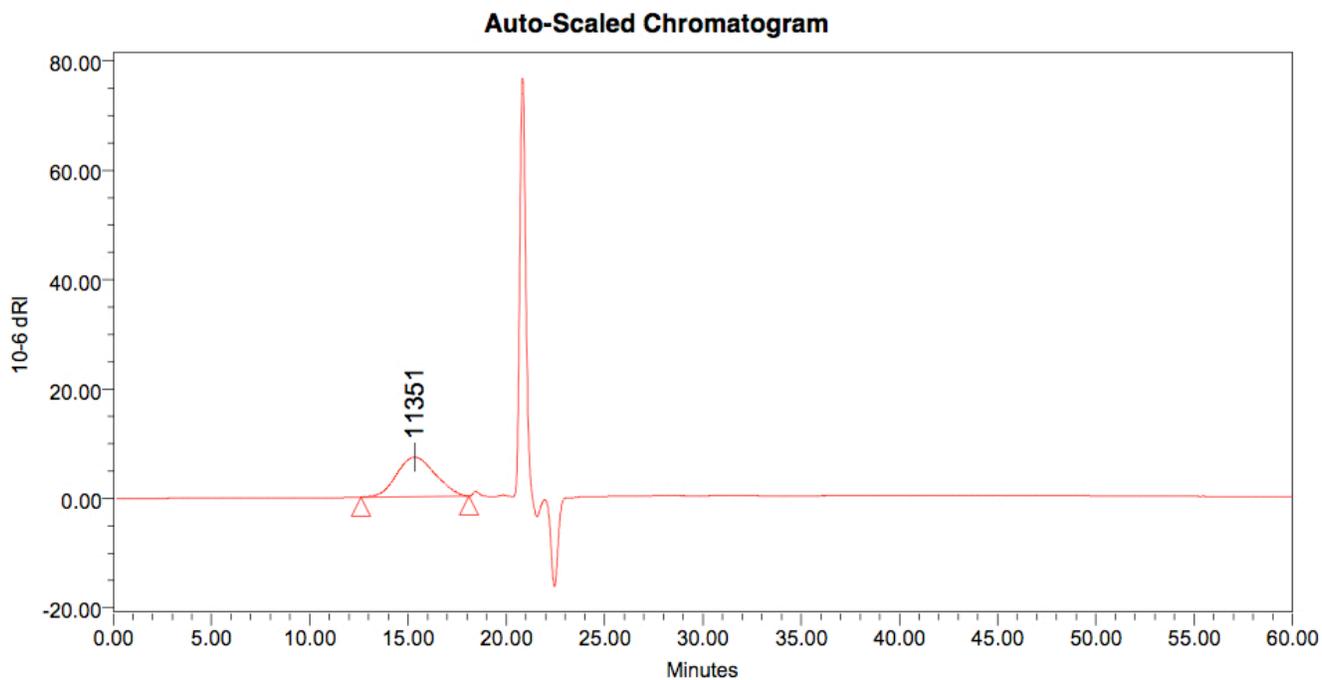
Figure S18. GPC Chromatogram of polydecylene acetal, 10 gram scale-up (Table S1, entry 10).



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	24569	60602	34477	115921	161307		2.466594		

Figure S19. GPC Chromatogram of polydecylene acetal, 50 gram scale-up (Table S1, entry 11).



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	7814	13030	11351	20379	29856		1.667630		

Figure S20. GPC Chromatogram of polydecylene acetal, first iteration (Table S1, entry 12).

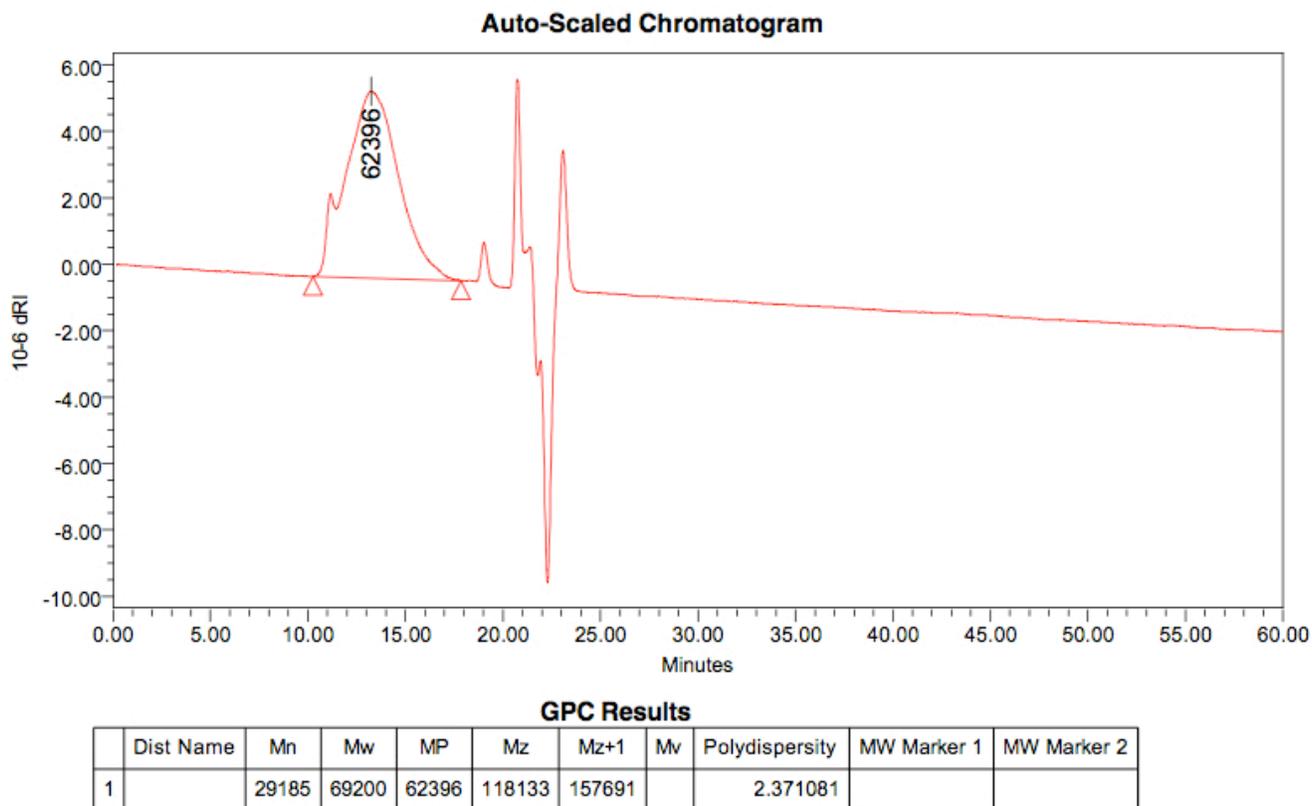


Figure S21. GPC Chromatogram of polydecylene acetal, *second iteration* (Table S1, entry 13).

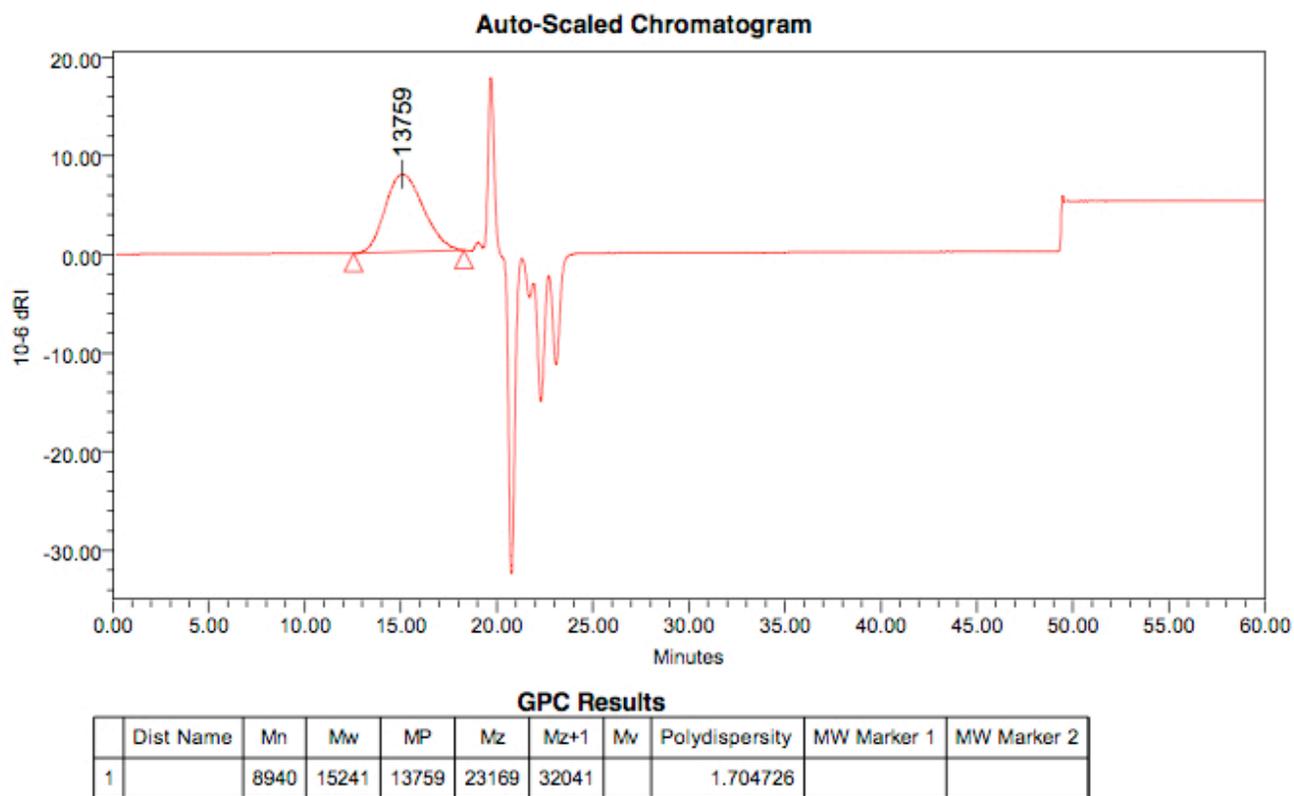


Figure S22. GPC Chromatogram of polydodecylene acetal, *first iteration* (Table S1, entry 14).

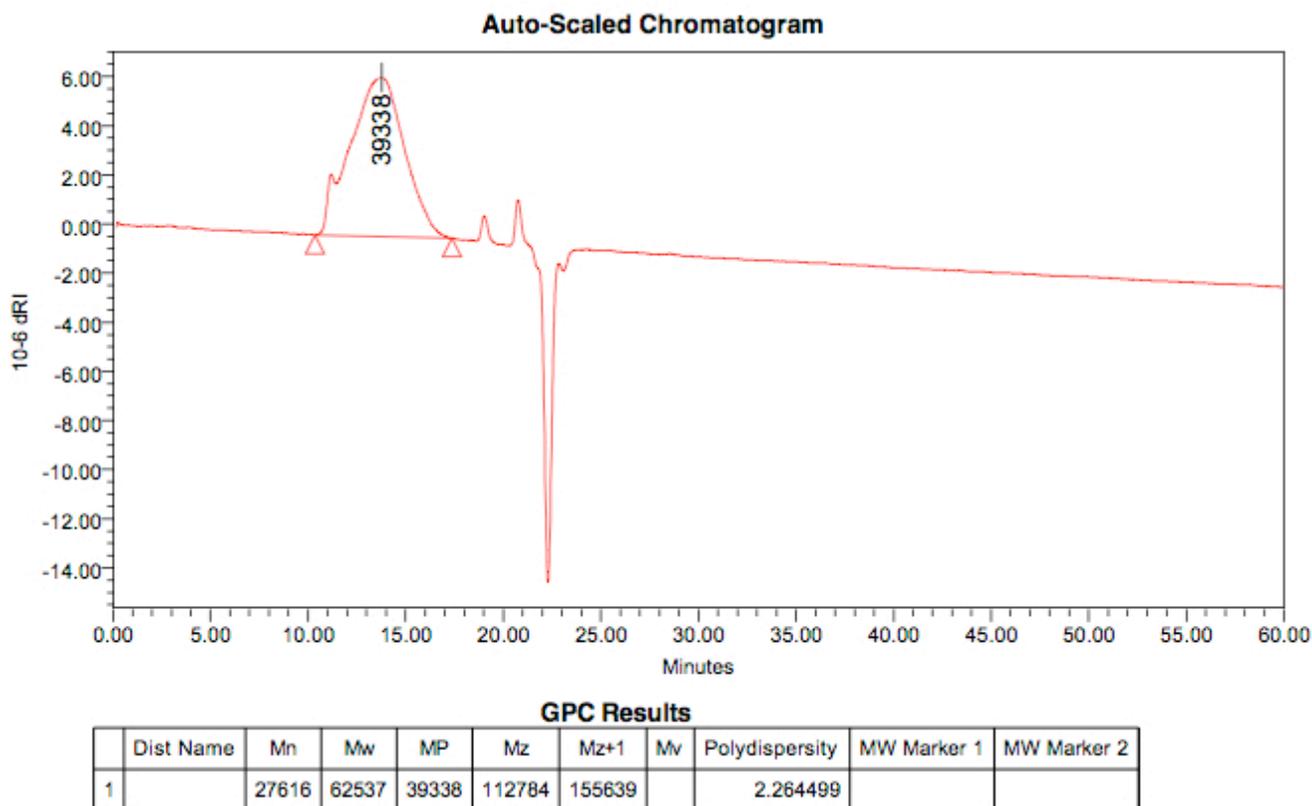


Figure S23. GPC Chromatogram of polydodecylene acetal, *second iteration* (Table S1, entry 15).

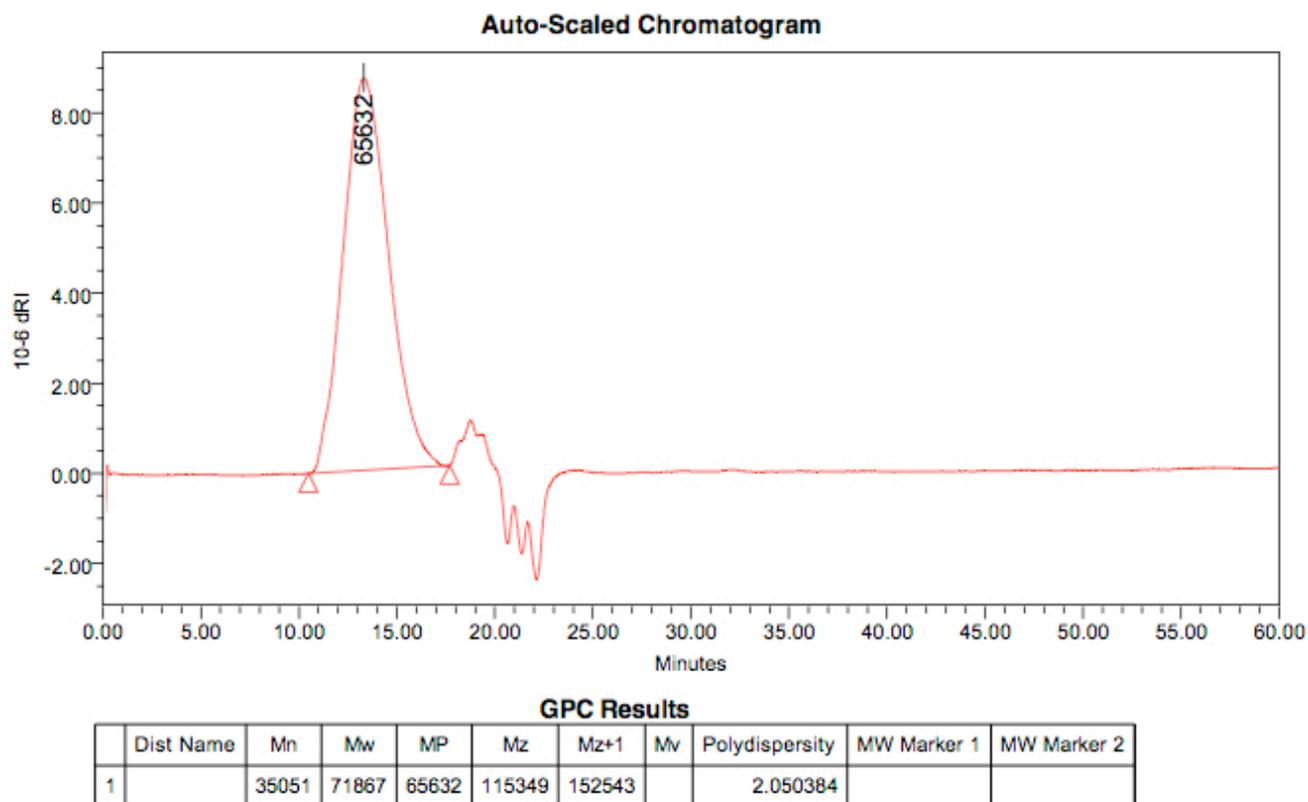


Figure S24. GPC Chromatogram of polydecylene acetal, *from dimethoxymethane* (Table S1, entry 16).

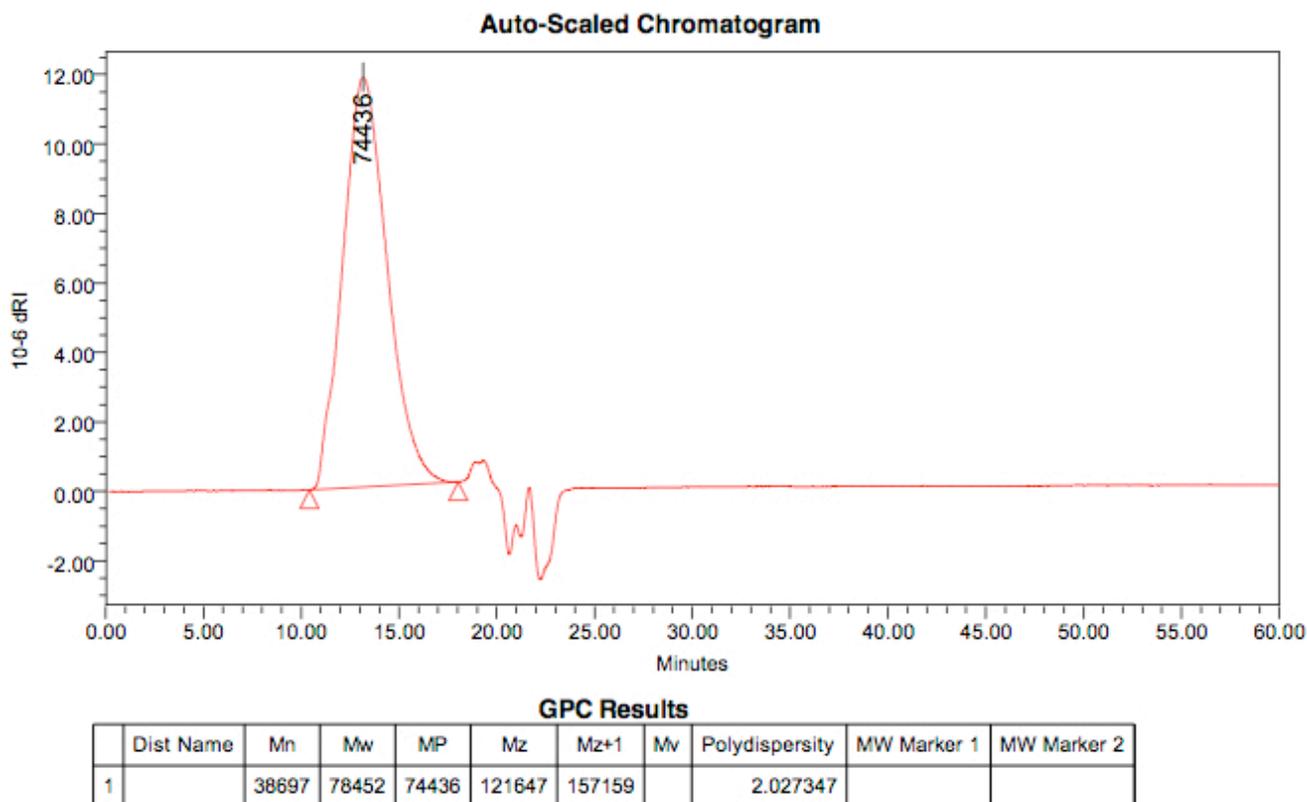


Figure S25. GPC Chromatogram of polydodecylene acetal, from dimethoxymethane (Table S1, entry 17).

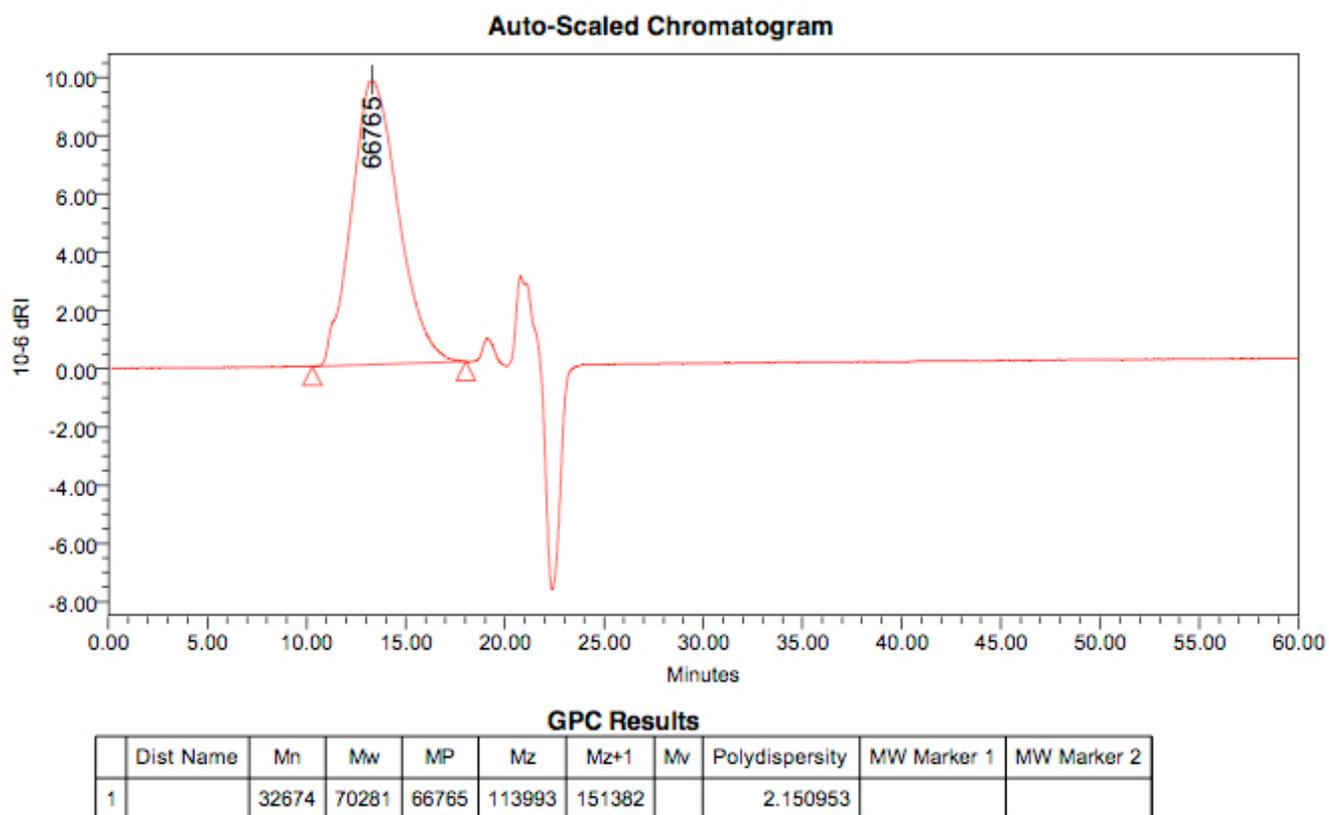


Figure S26. GPC Chromatogram of polydecylene acetal, from diethoxymethane:diol = 2:1 (Table S1, entry 18).

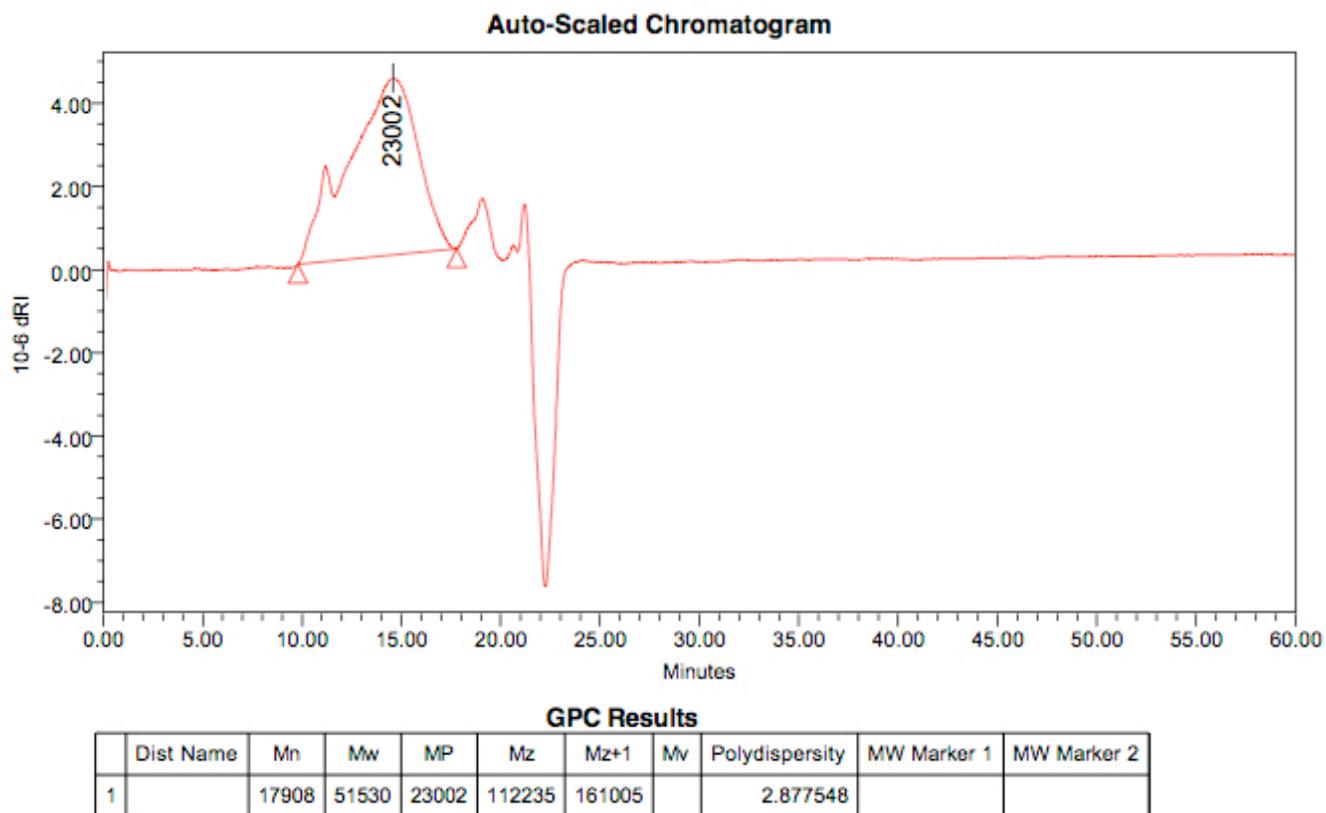


Figure S27. GPC Chromatogram of polydecylene acetal, from dimethoxymethane:diol = 2:1 (Table S1, entry 19).

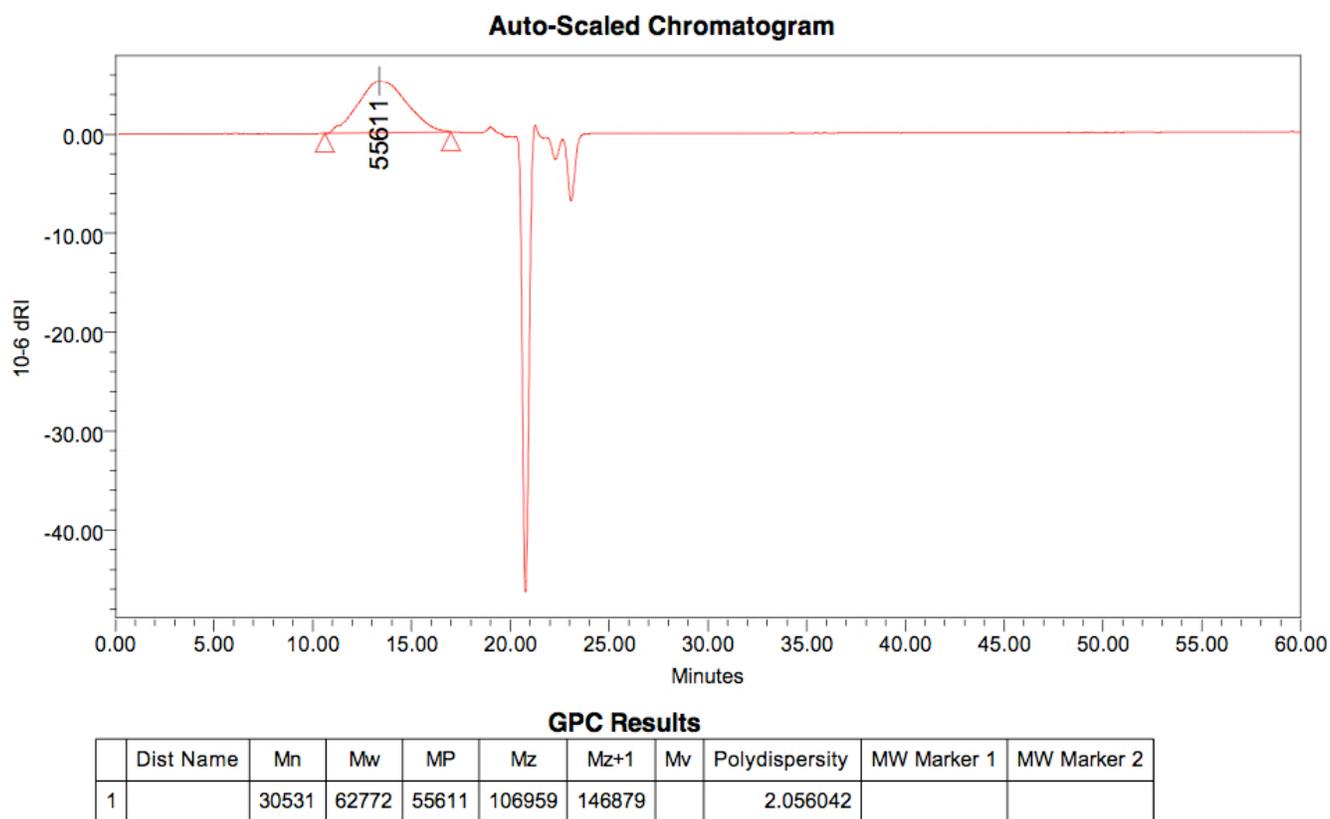


Figure S28. GPC Chromatogram of pure polydecylene acetal (PDA) [Degradation at t=0 hours].

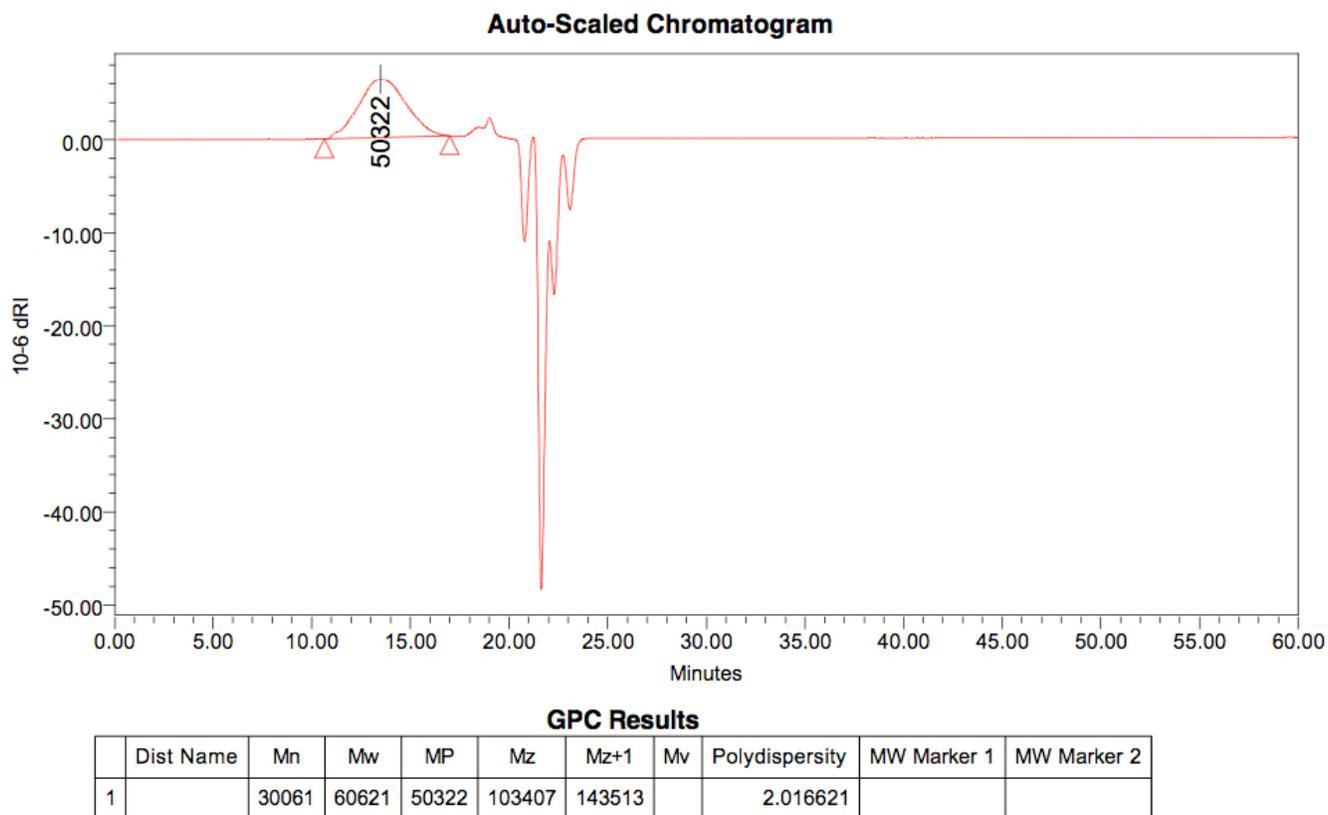


Figure S29. GPC Chromatogram of polydecylene acetal (PDA) [Degradation at t=3 hours].

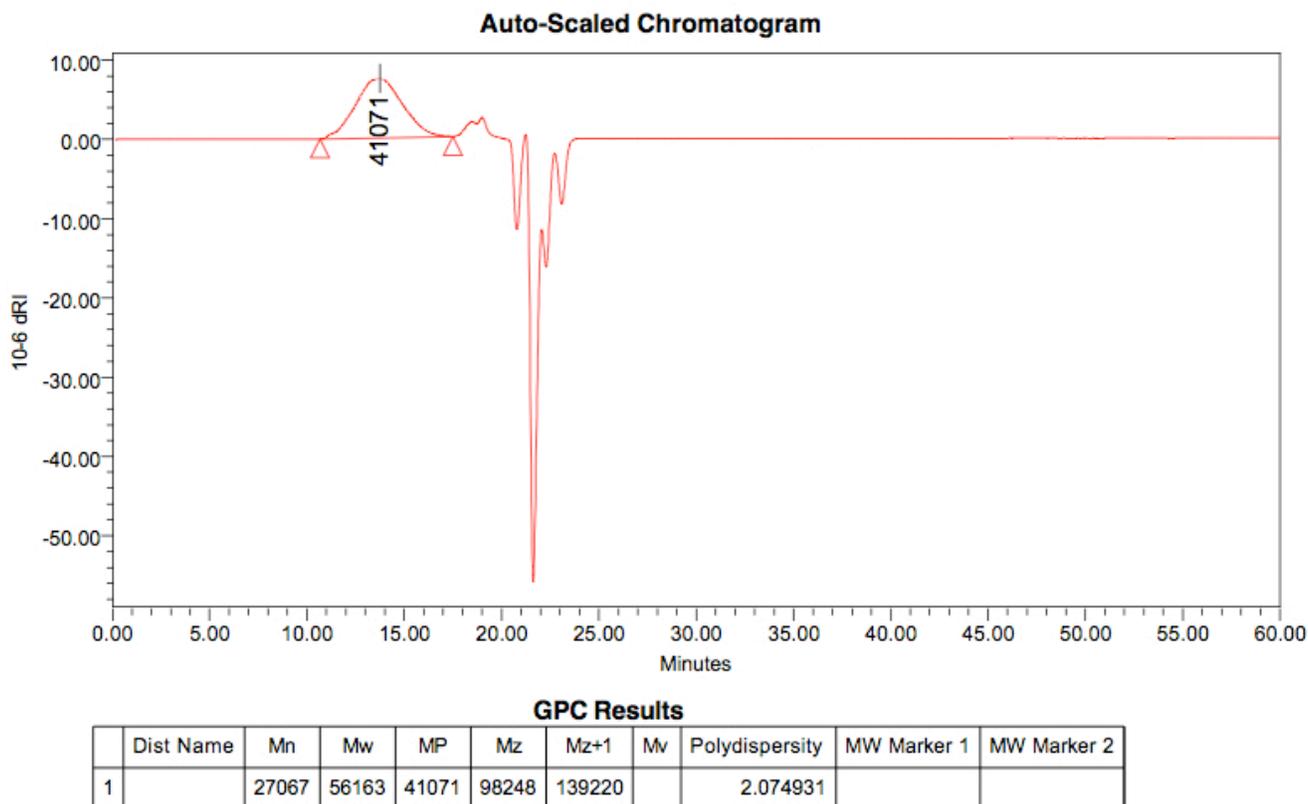


Figure S30. GPC Chromatogram of polydecylene acetal (PDA) [Degradation at t=9 hours].

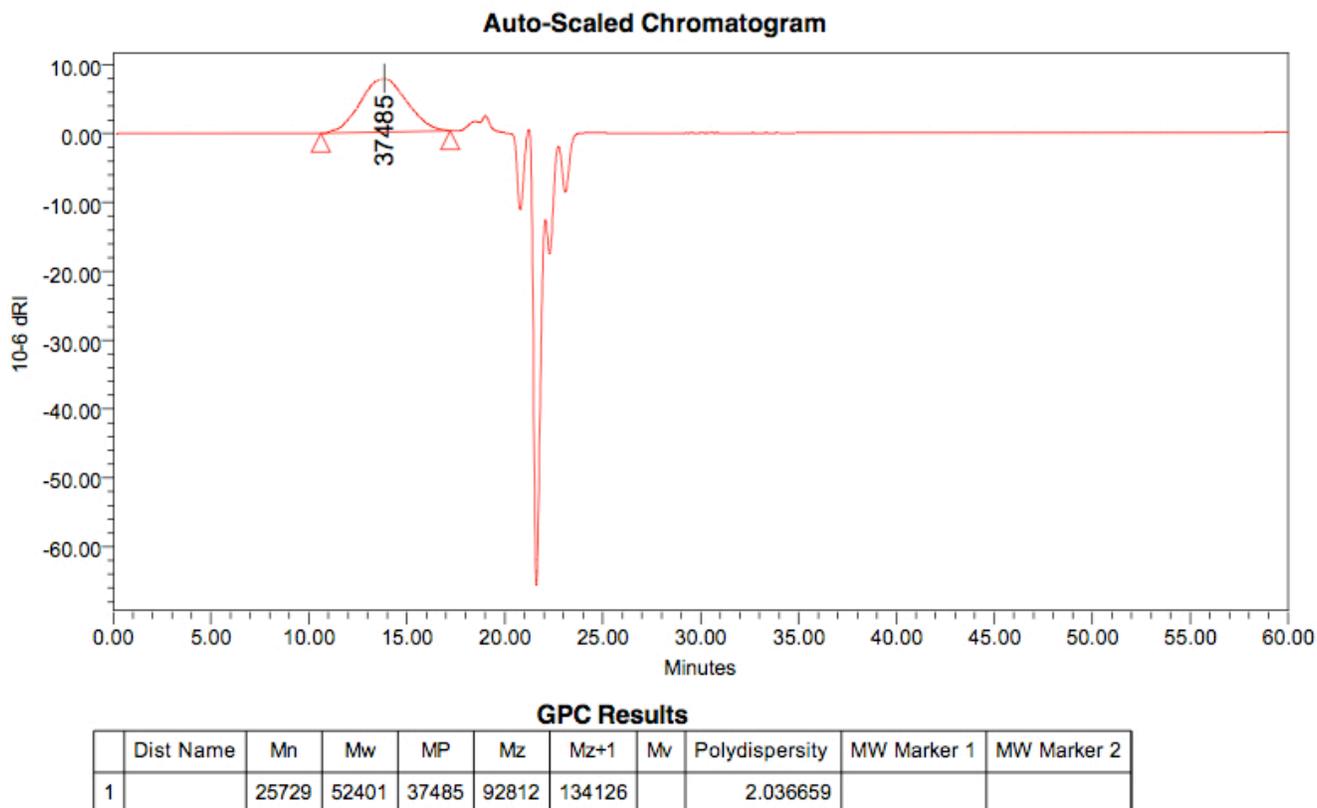


Figure S31. GPC Chromatogram of polydecylene acetal (PDA) [Degradation at t=15 hours].

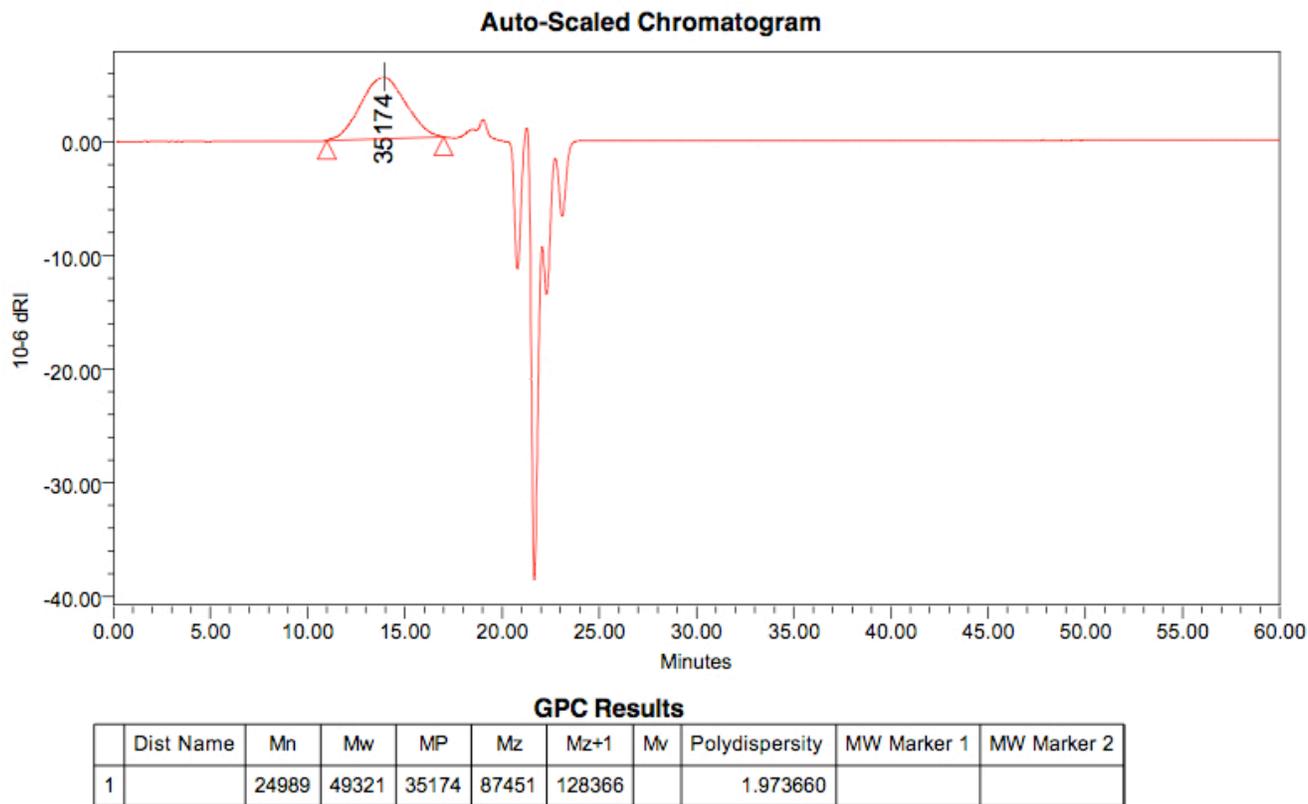
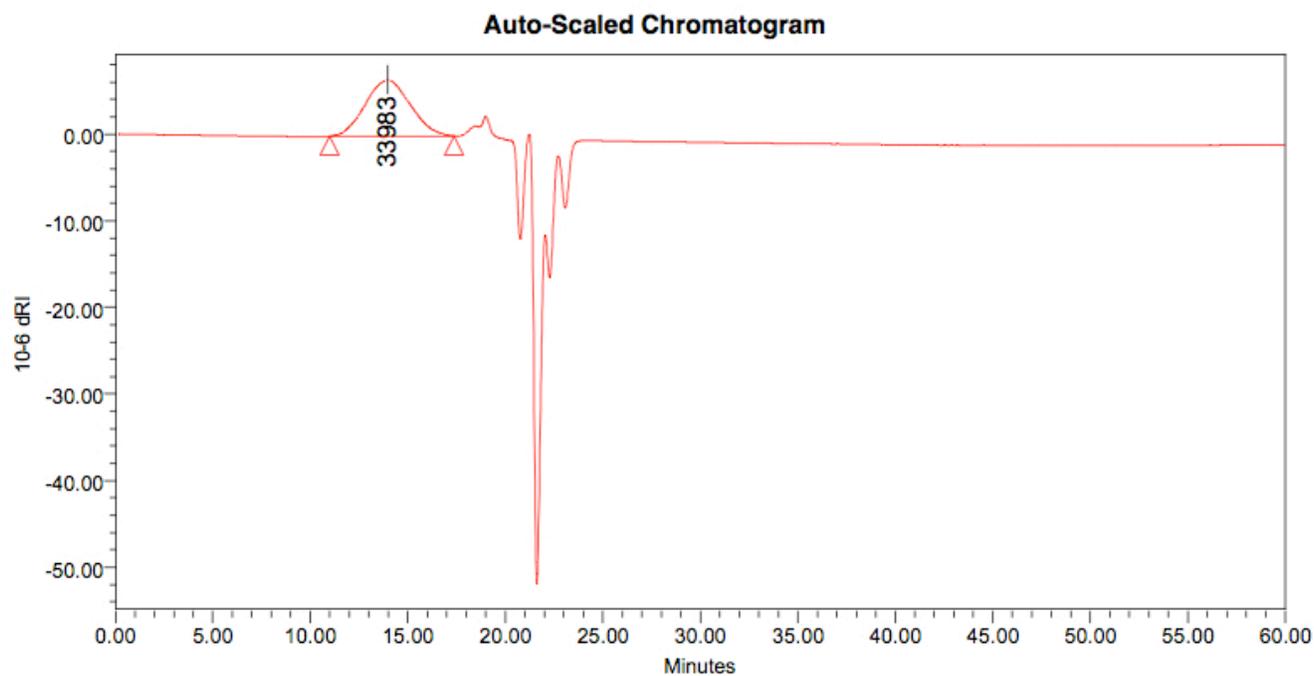


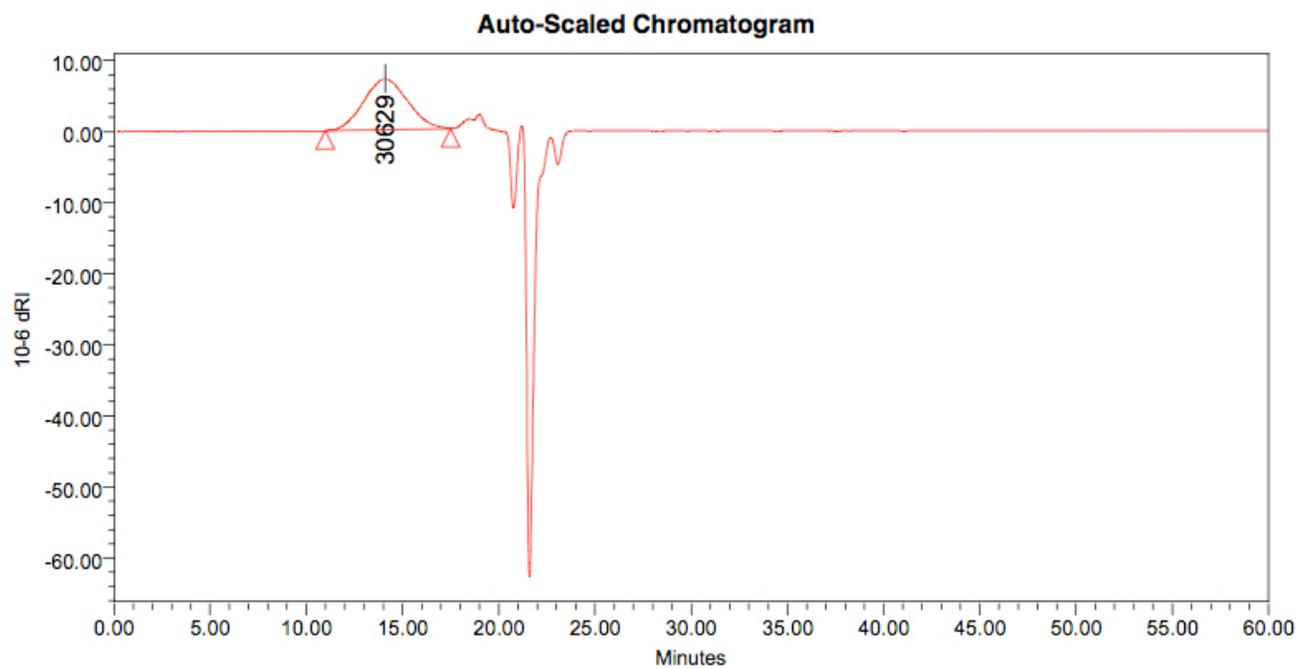
Figure S32. GPC Chromatogram of polydecylene acetal (PDA) [Degradation at t=21 hours].



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		22990	46350	33983	83450	124537		2.016058		

Figure S33. GPC Chromatogram of polydecylene acetal (PDA) [Degradation at t=27 hours]



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		20416	41368	30629	76006	116941		2.026213		

Figure S34. GPC Chromatogram of polydecylene acetal (PDA) [Degradation at t=39 hours]

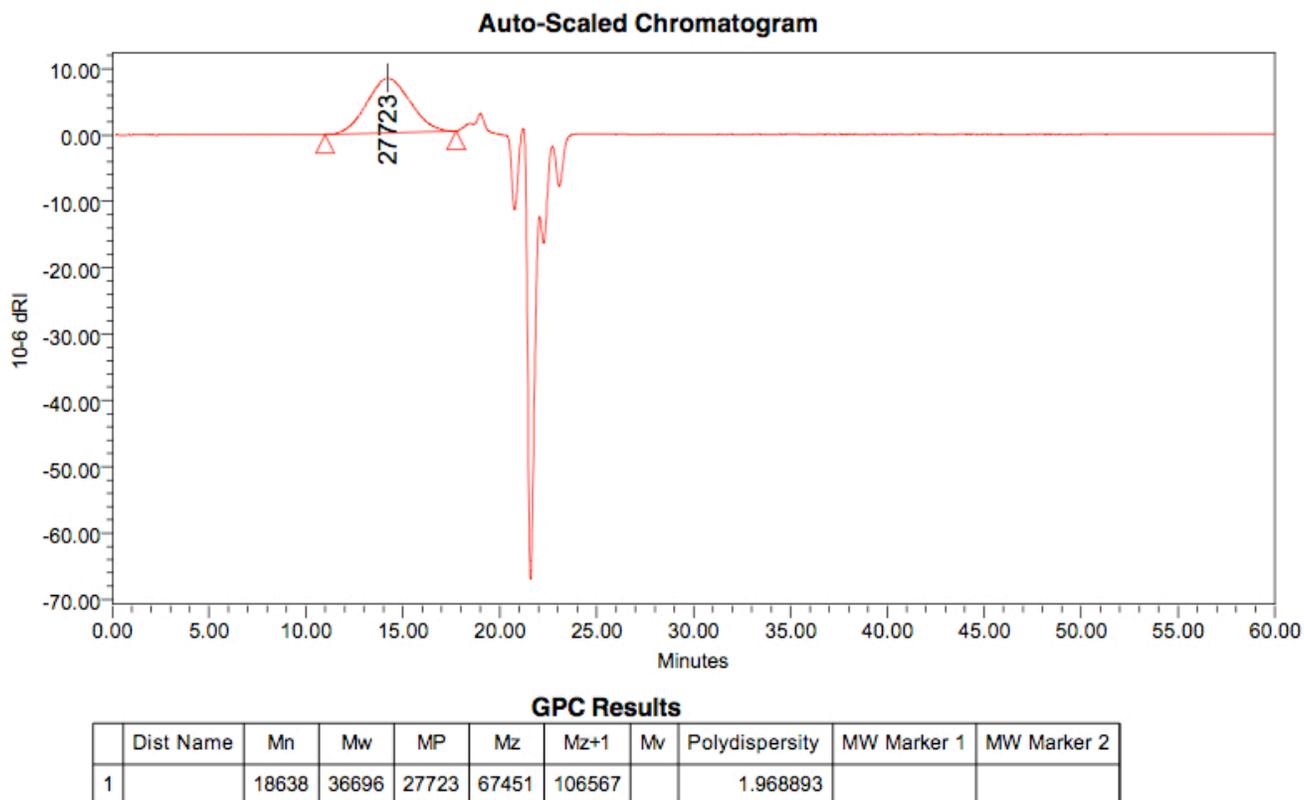


Figure S35. GPC Chromatogram of polydecylene acetal (PDA) [Degradation at t=51 hours].

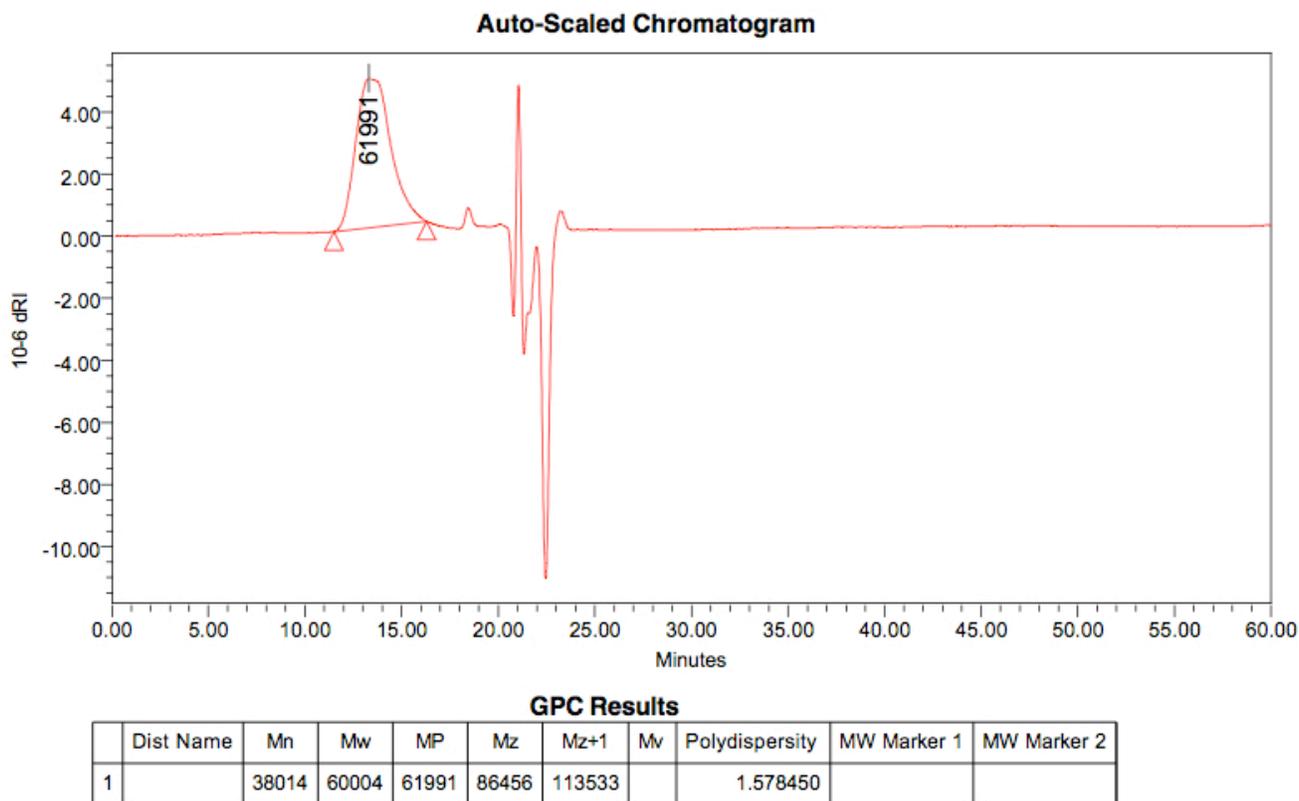


Figure S36. GPC Chromatogram of pure poly-L-lactide (PLLA) [Degradation at t=0 hours].

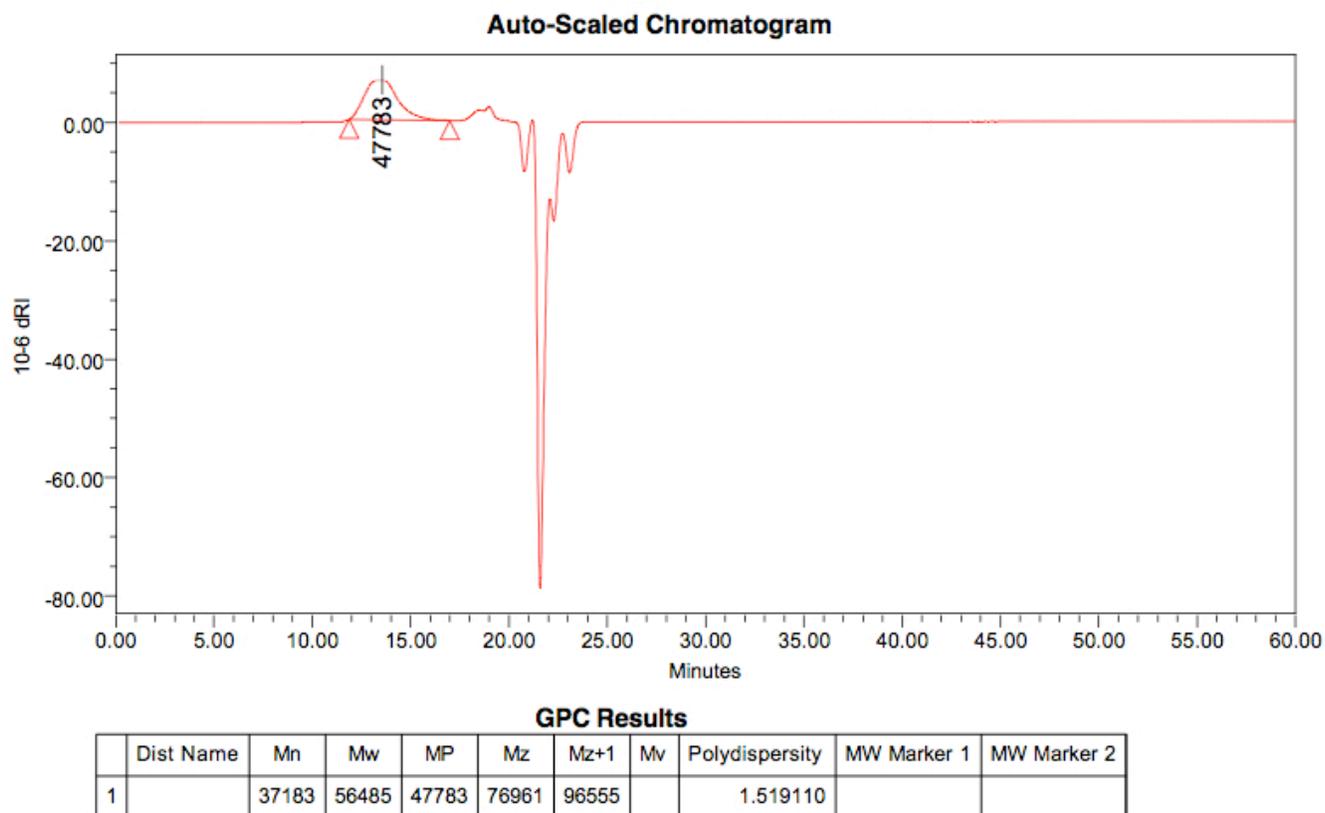


Figure S37. GPC Chromatogram of poly-L-lactide (PLLA) [Degradation at t=3 hours].

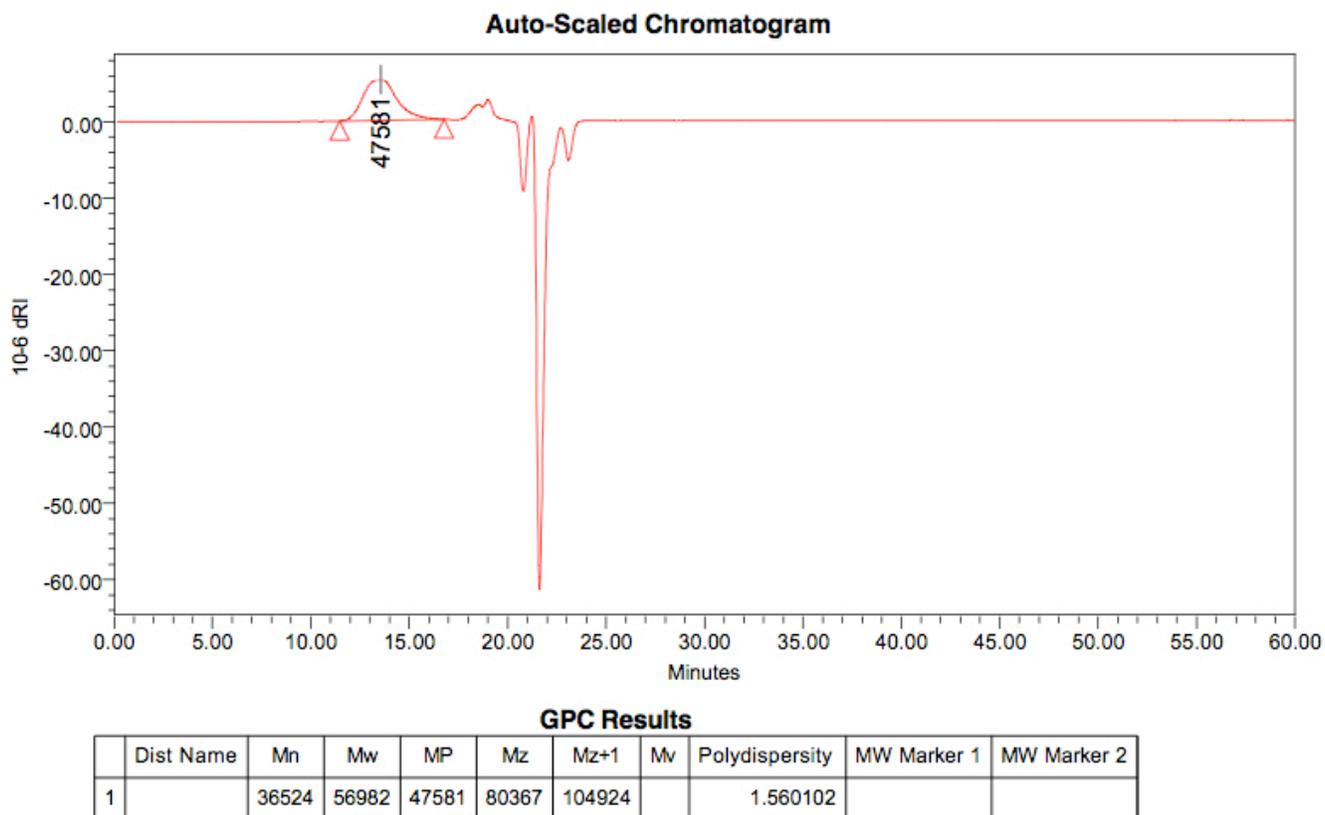
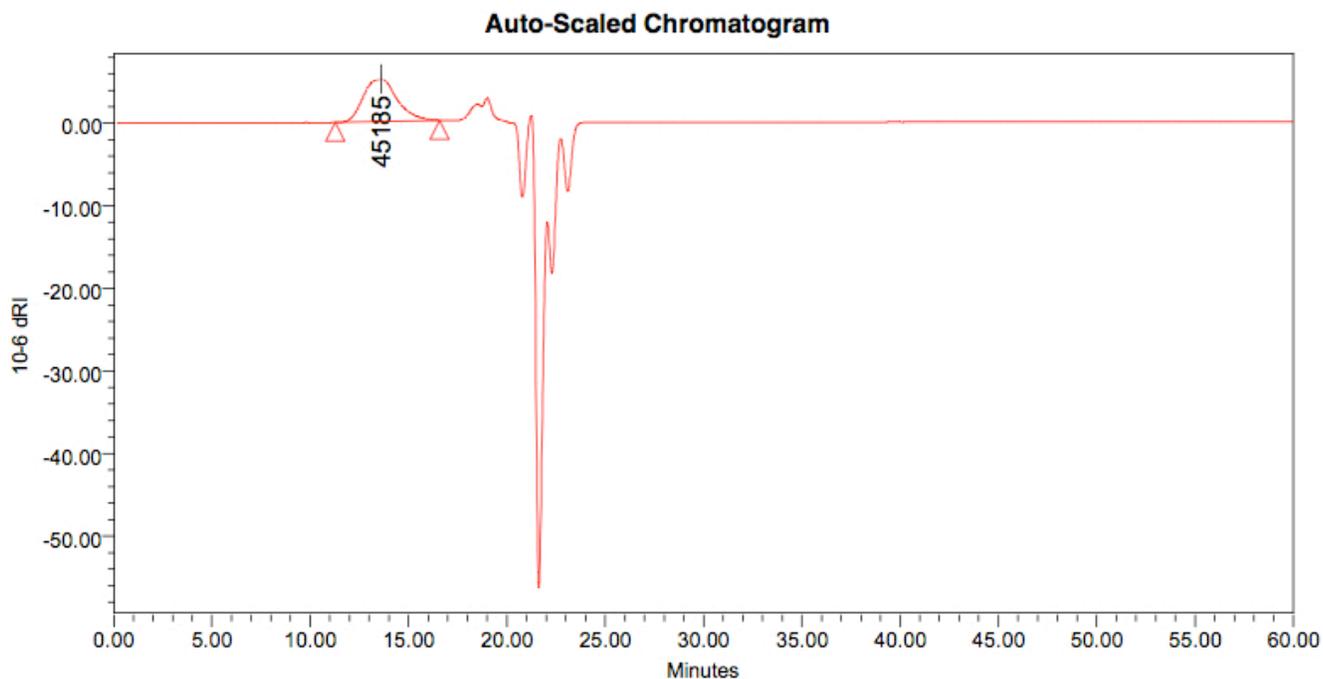


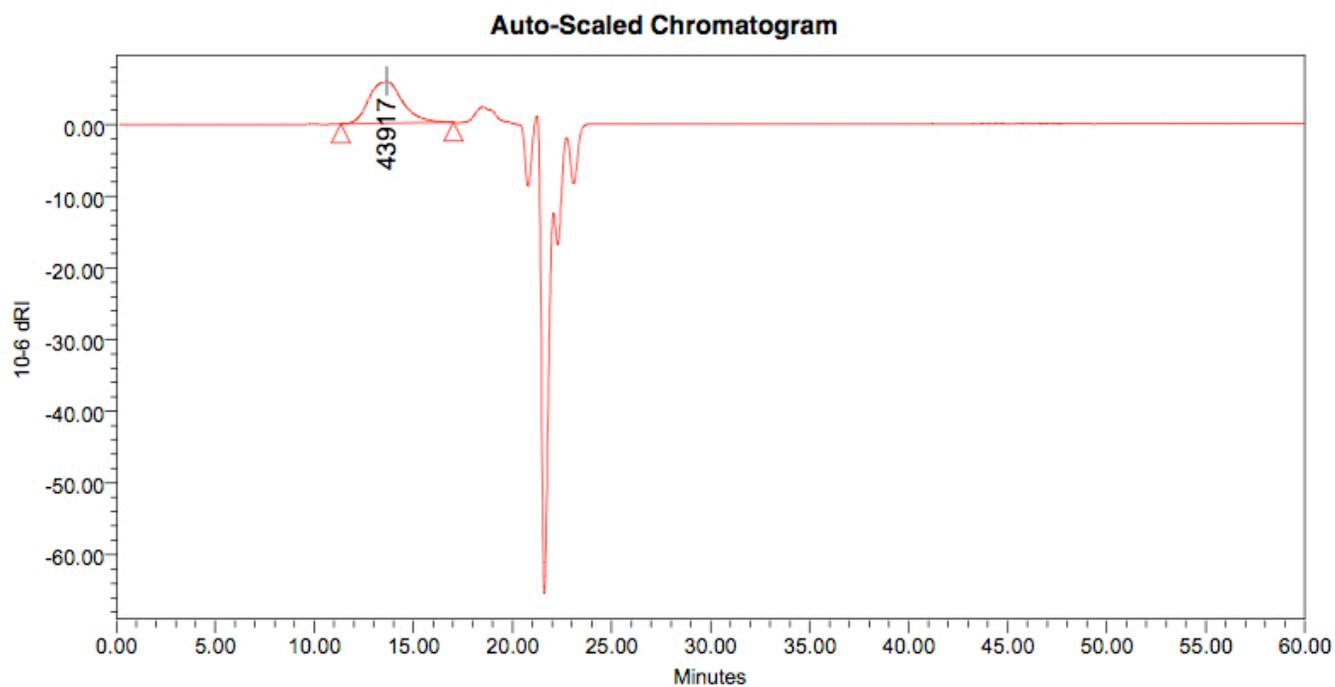
Figure S38. GPC Chromatogram of poly-L-lactide (PLLA) [Degradation at t=9 hours].



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	35821	55151	45185	77828	101908		1.539611		

Figure S39. GPC Chromatogram of poly-L-lactide (PLLA) [Degradation at t=15 hours].



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	33453	52932	43917	75402	99917		1.582266		

Figure S40. GPC Chromatogram of poly-L-lactide (PLLA) [Degradation at t=21 hours].

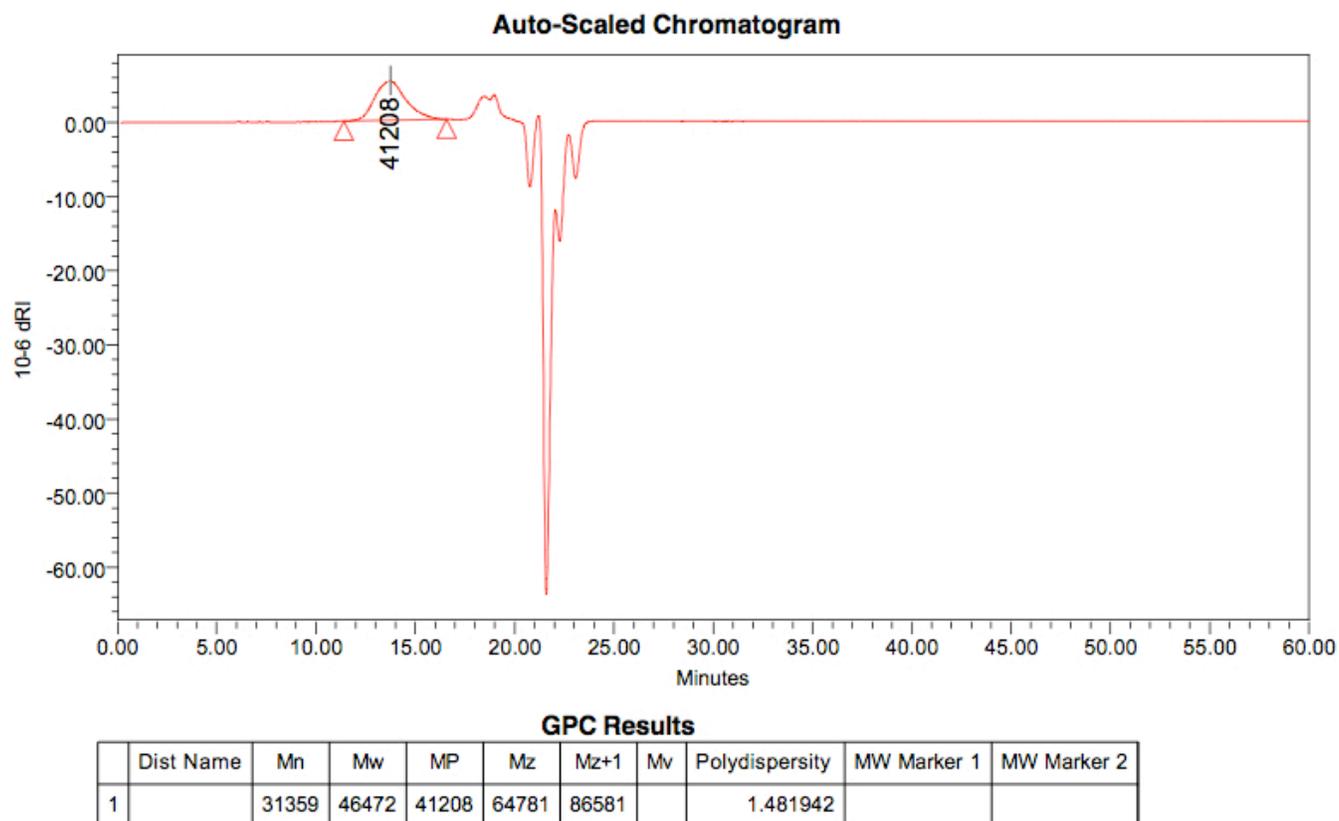


Figure S41. GPC Chromatogram of poly-L-lactide (PLLA) [Degradation at t=27 hours].

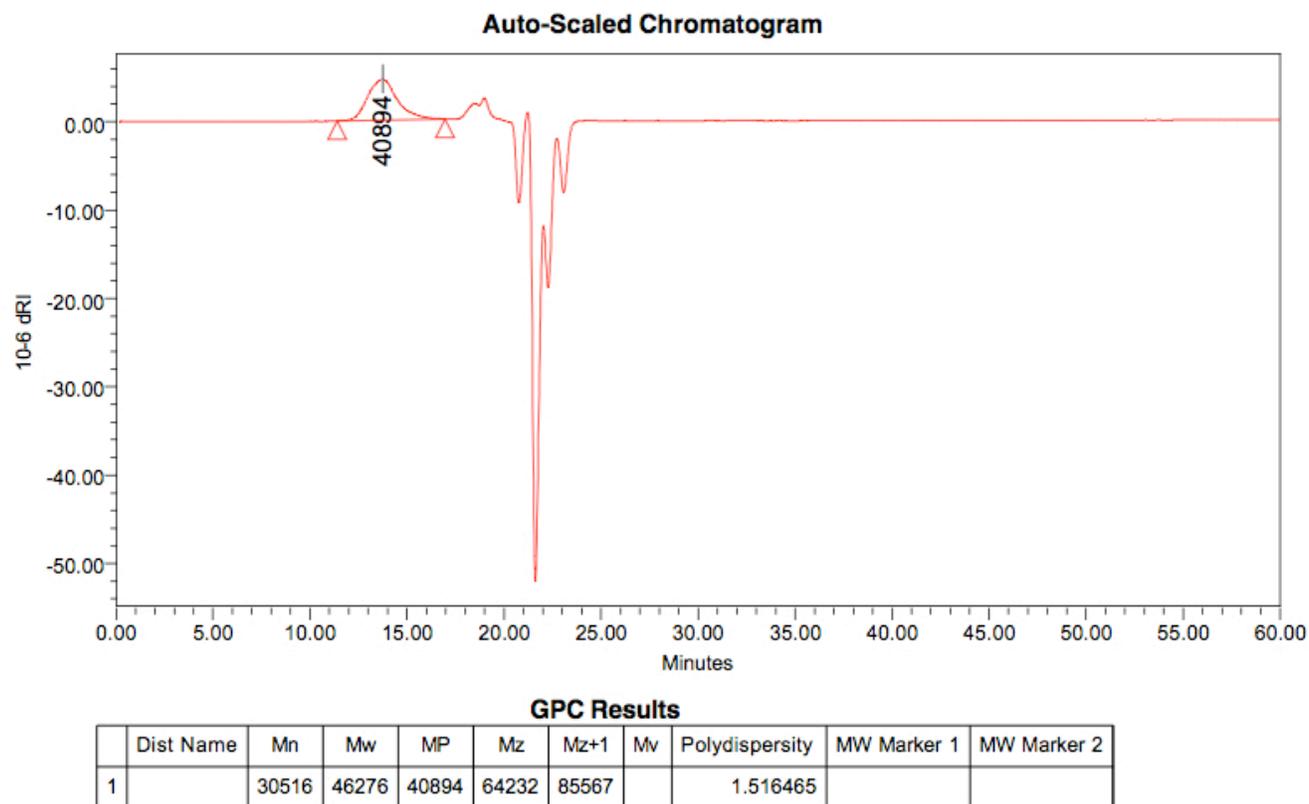
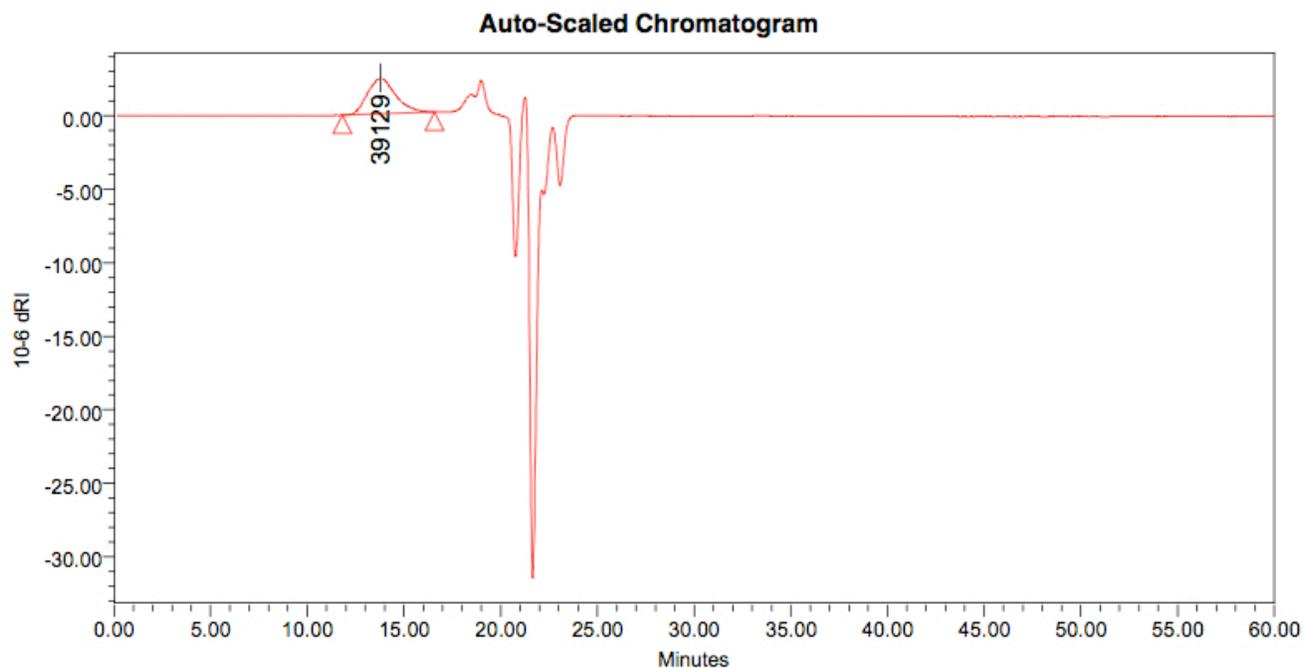


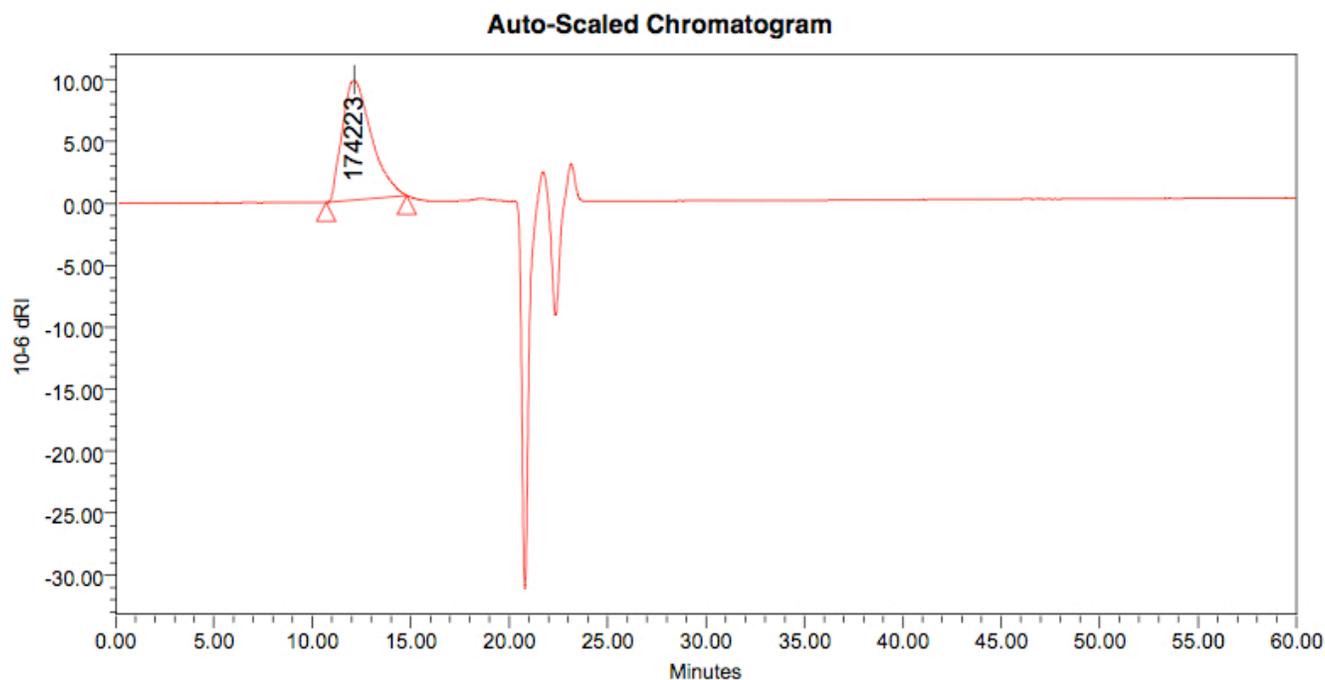
Figure S42. GPC Chromatogram of poly-L-lactide (PLLA) [Degradation at t=39 hours].



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		29461	41663	39129	55129	69654		1.414177		

Figure S43. GPC Chromatogram of poly-L-lactide (PLLA) [Degradation at t=51 hours].



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		95752	131265	174223	161021	182674		1.370881		

Figure S44. GPC Chromatogram of pure NatureWorks PLA (PLA-600) [Degradation at t=0 hours].

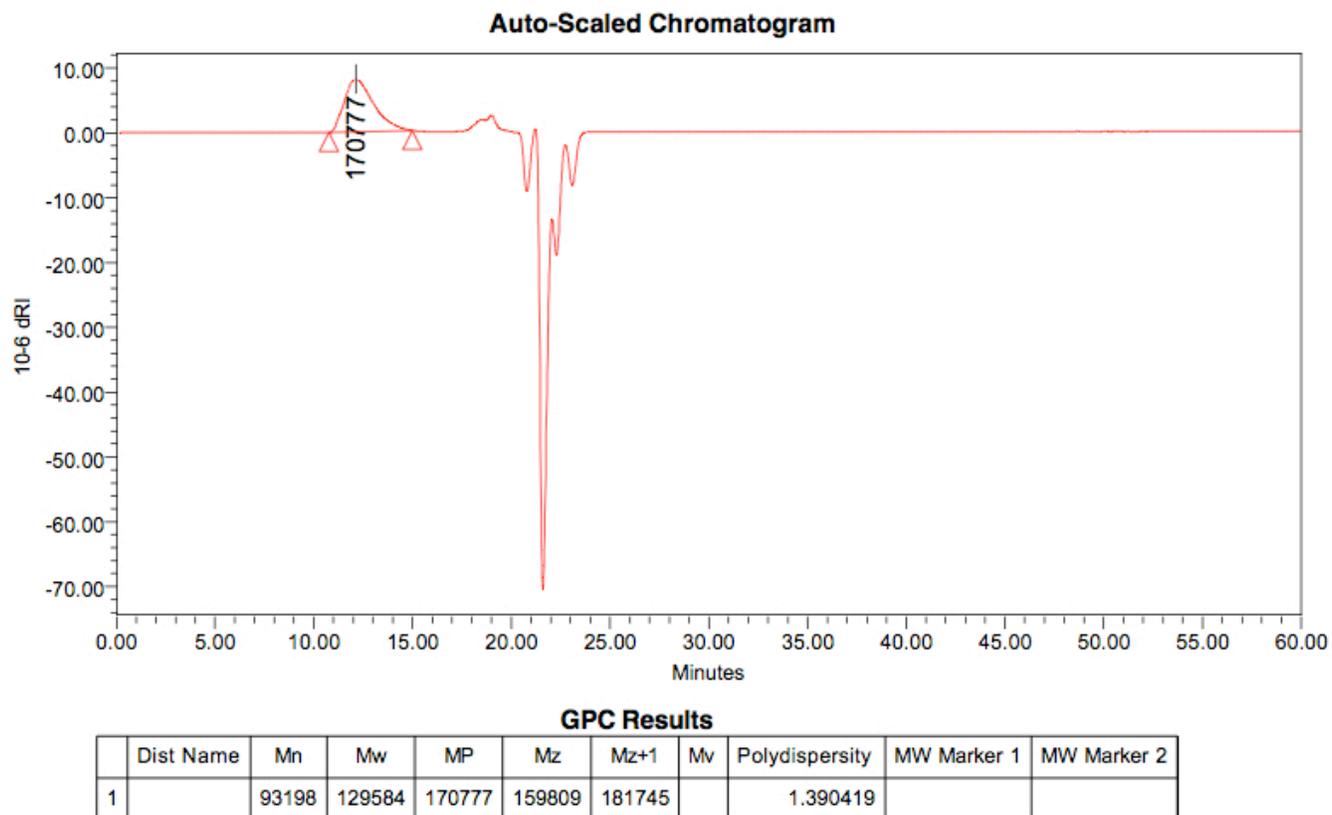


Figure S45. GPC Chromatogram of NatureWorks PLA (PLA-600) [Degradation at t=3 hours].

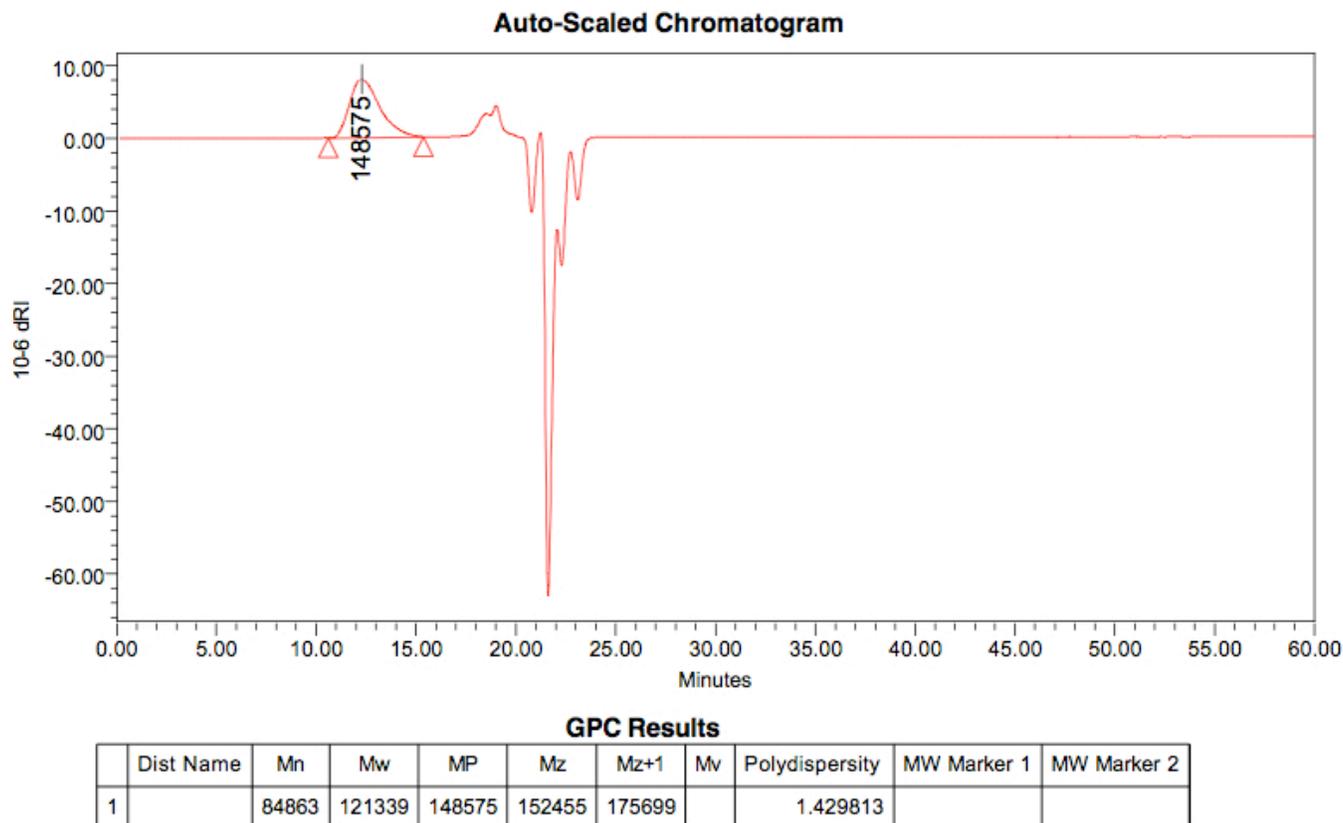
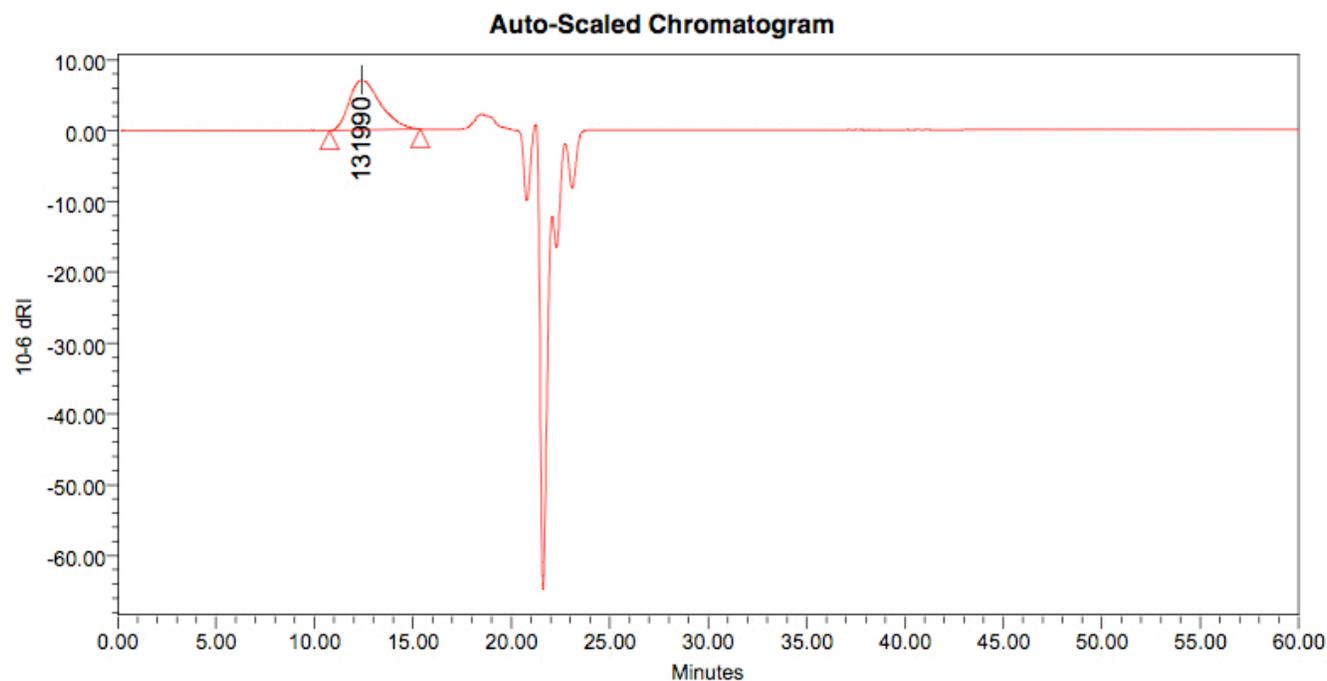


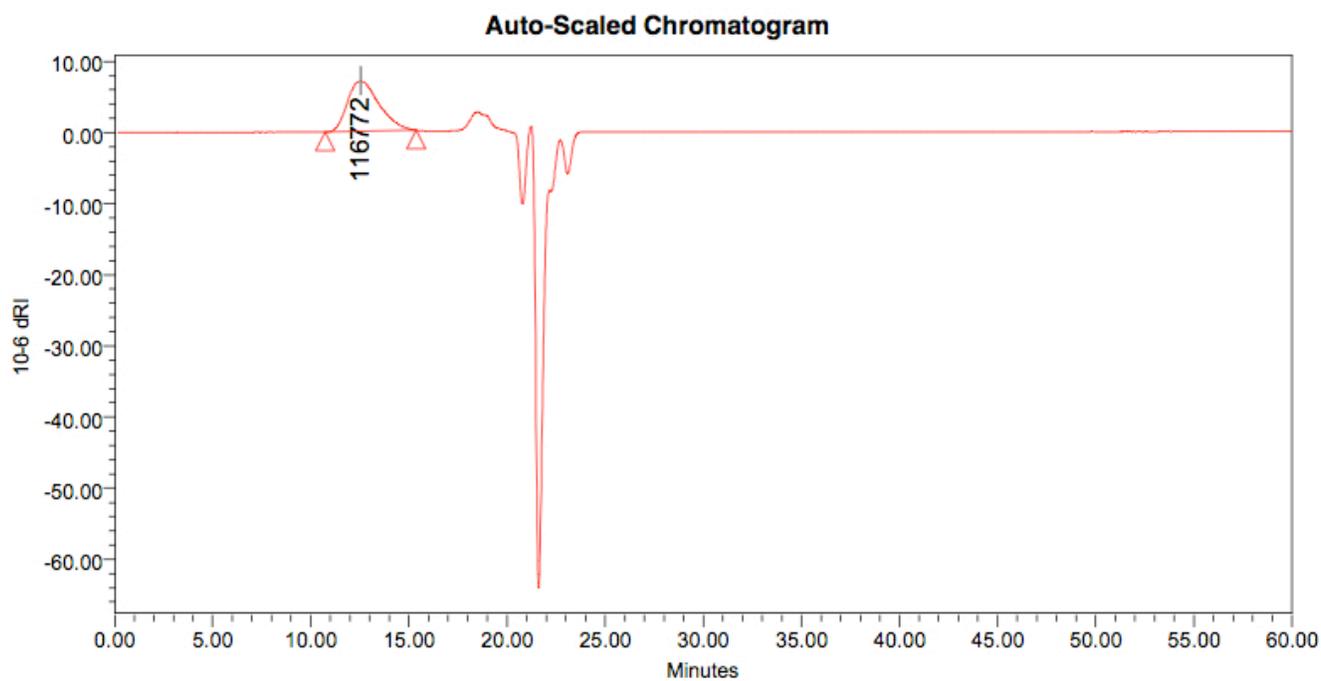
Figure S46. GPC Chromatogram of NatureWorks PLA (PLA-600) [Degradation at t=9 hours].



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	77666	112917	131990	145022	169867		1.453877		

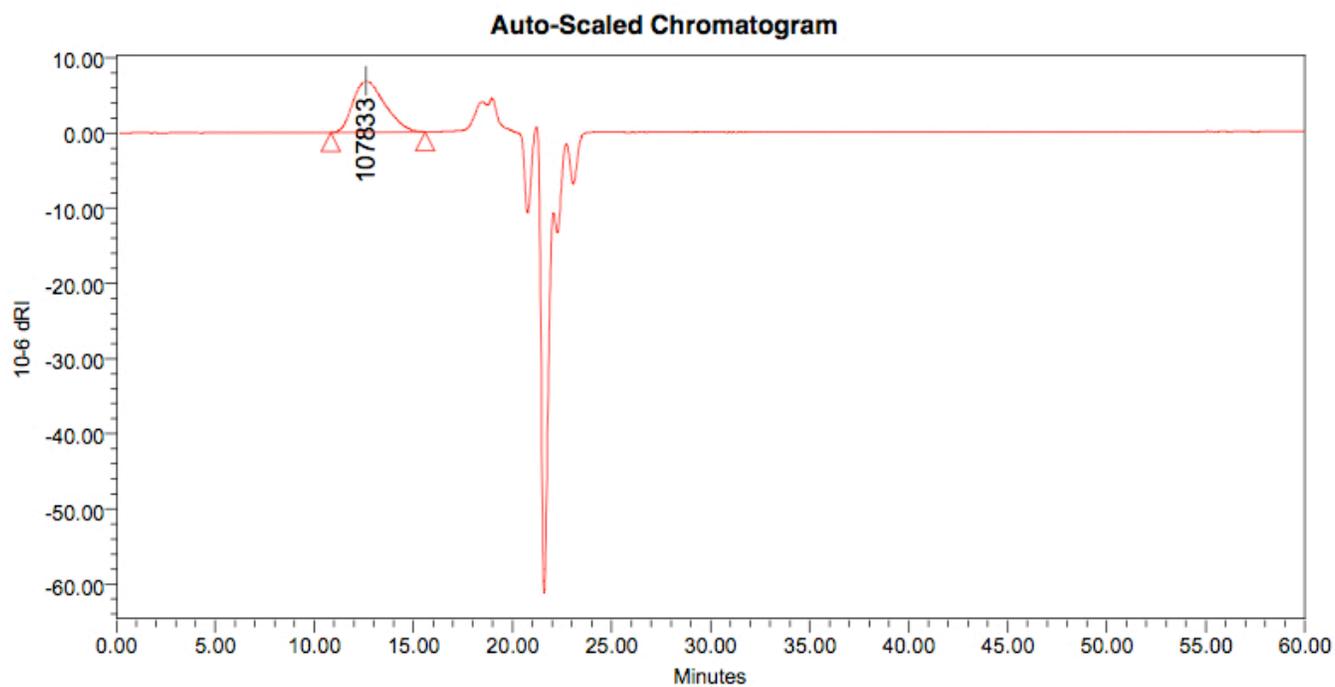
Figure S47. GPC Chromatogram of NatureWorks PLA (PLA-600) [Degradation at t=15 hours].



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	71660	105422	116772	137833	163881		1.471142		

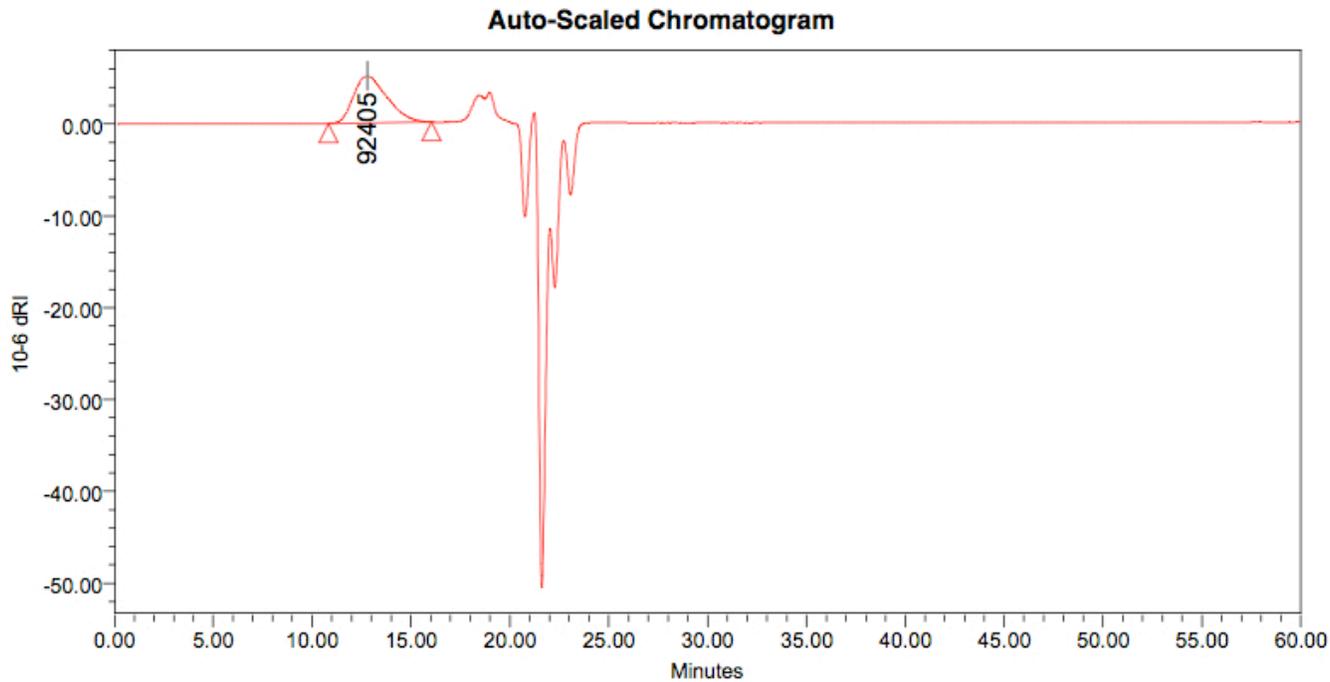
Figure S48. GPC Chromatogram of NatureWorks PLA (PLA-600) [Degradation at t=21 hours].



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	69000	100840	107833	132768	159354		1.461454		

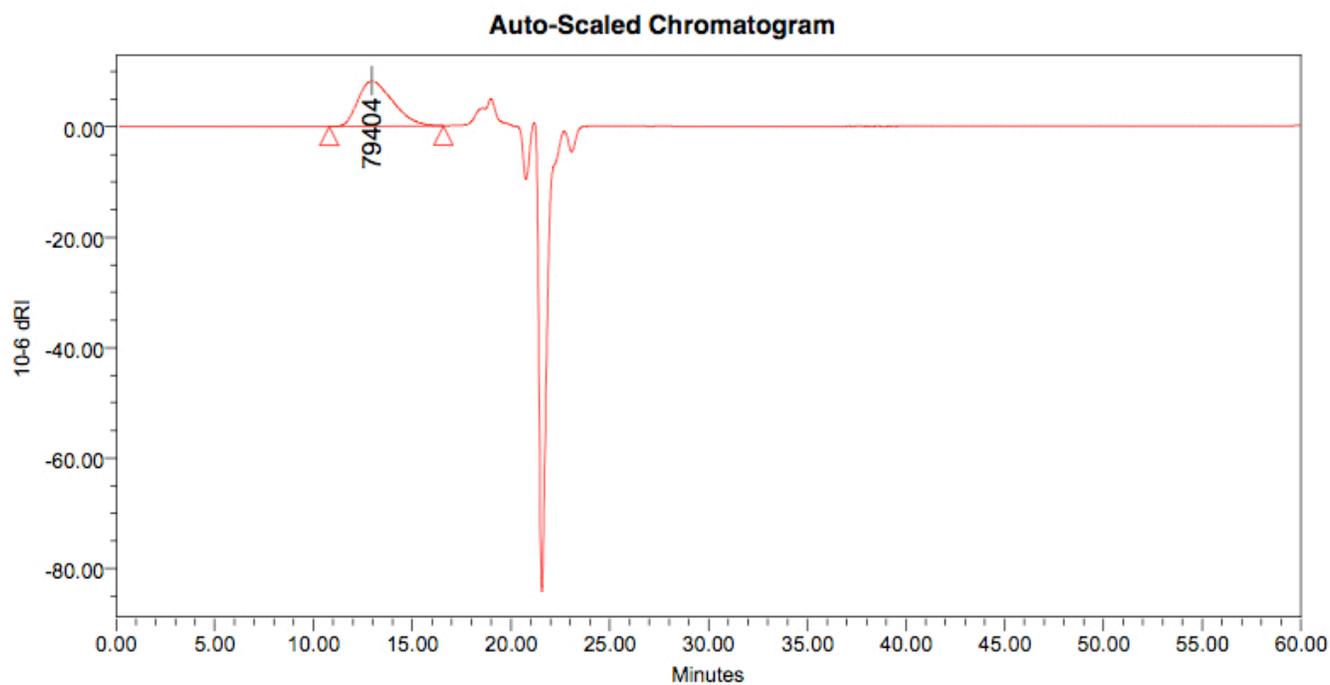
Figure S49. GPC Chromatogram of NatureWorks PLA (PLA-600) [Degradation at t=27 hours].



GPC Results

Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	56067	87837	92405	120662	148869		1.566643		

Figure S50. GPC Chromatogram of NatureWorks PLA (PLA-600) [Degradation at t=39 hours].



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		47171	76650	79404	108583	137489		1.624932		

Figure S51. GPC Chromatogram of NatureWorks PLA (PLA-600) [Degradation at t=51 hours].

Differential Scanning Calorimetry (DSC) Thermograms

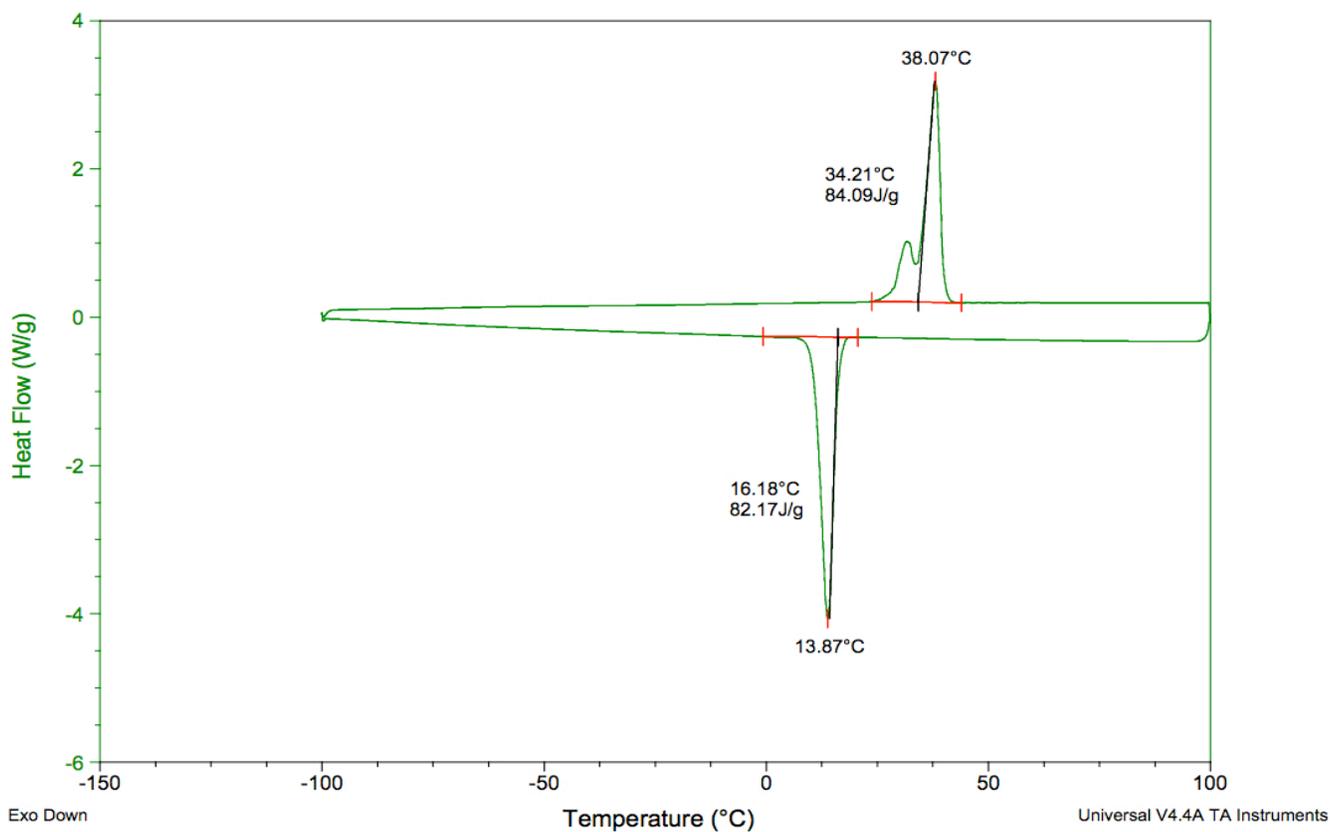


Figure S52. DSC Thermogram of poly(pentylene acetal) (Table S1, entry 1).

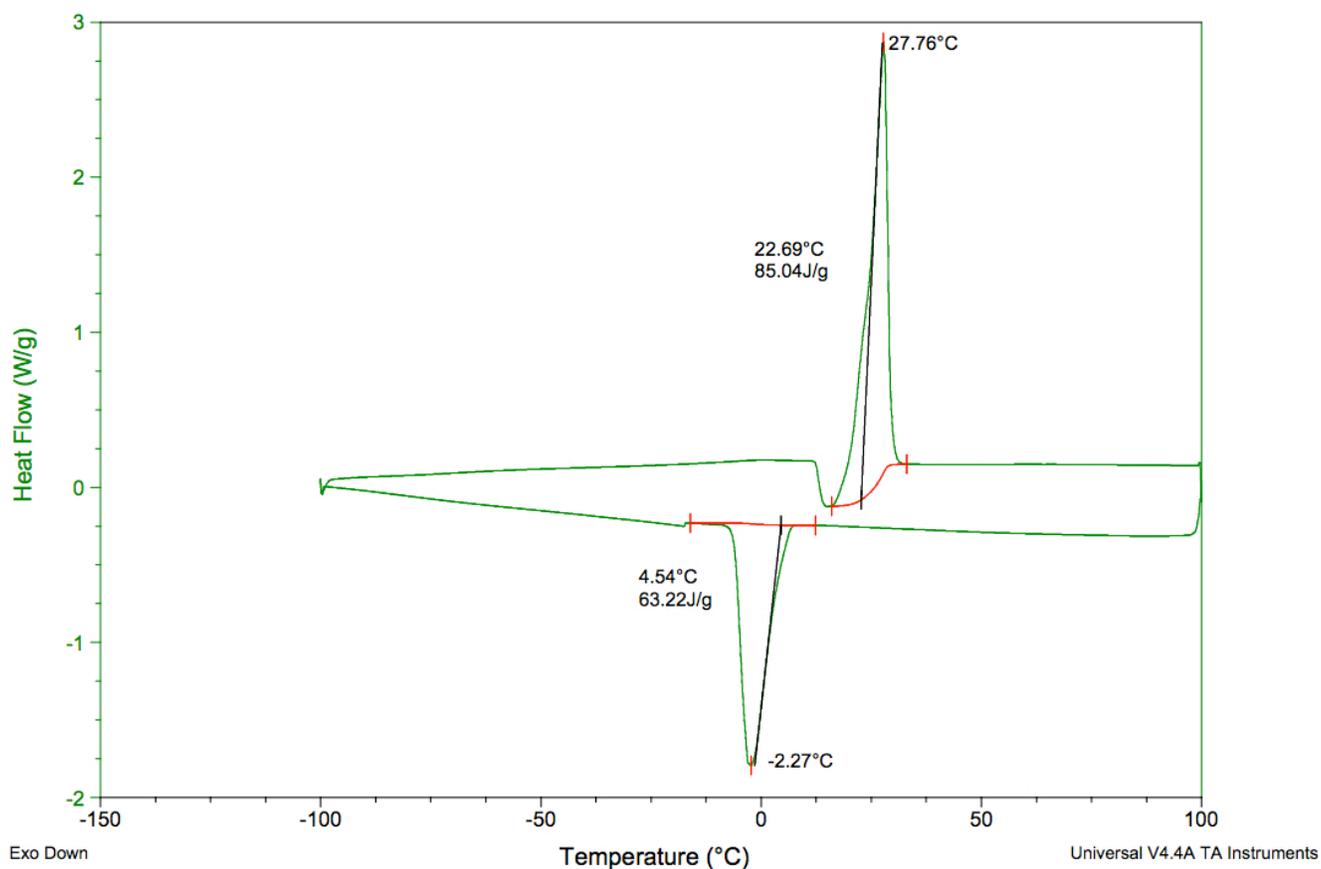


Figure S53. DSC Thermogram of poly(hexylene acetal) (Table S1, entry 2).

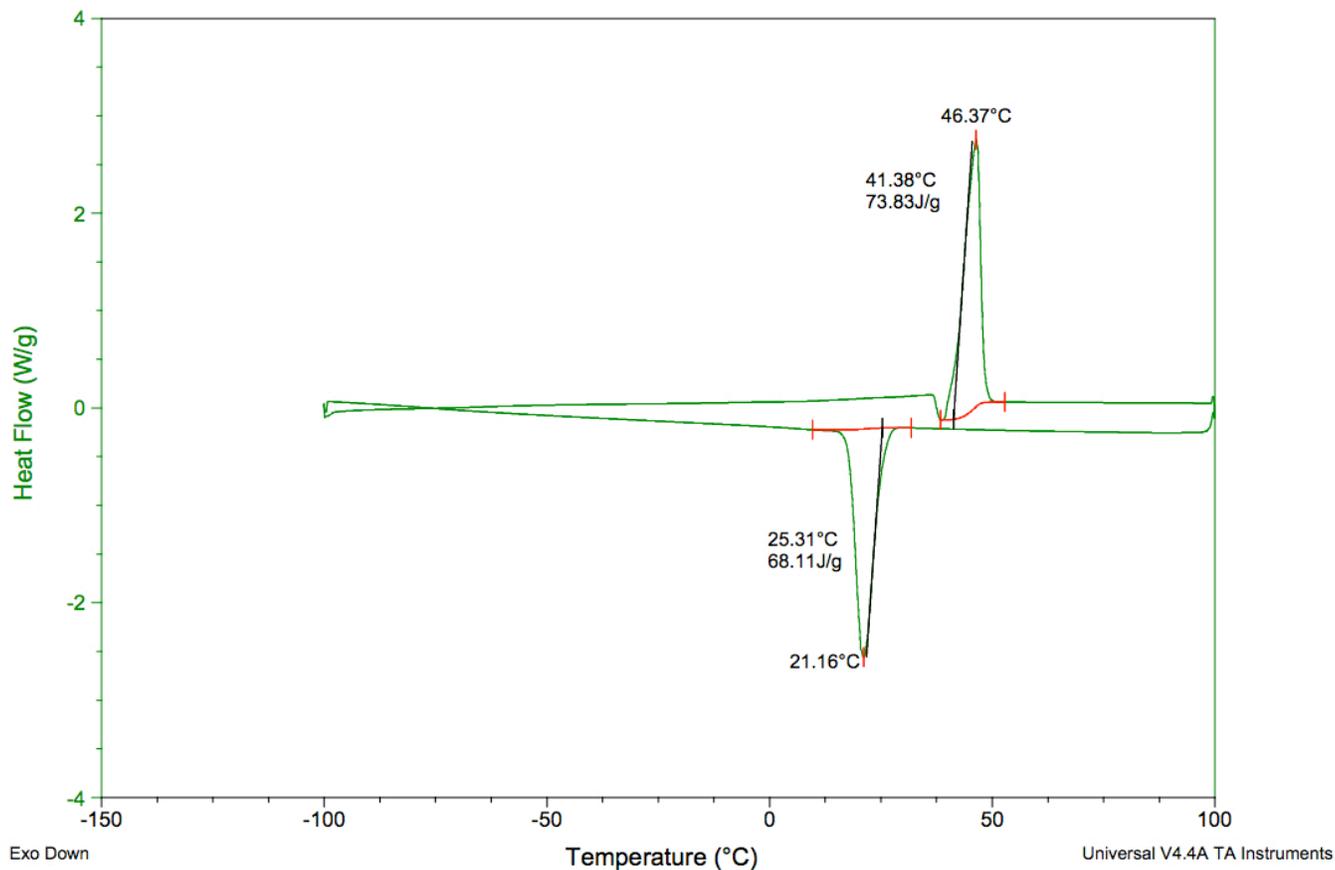


Figure S54. DSC Thermogram of polyheptylene acetal (Table S1, entry 3).

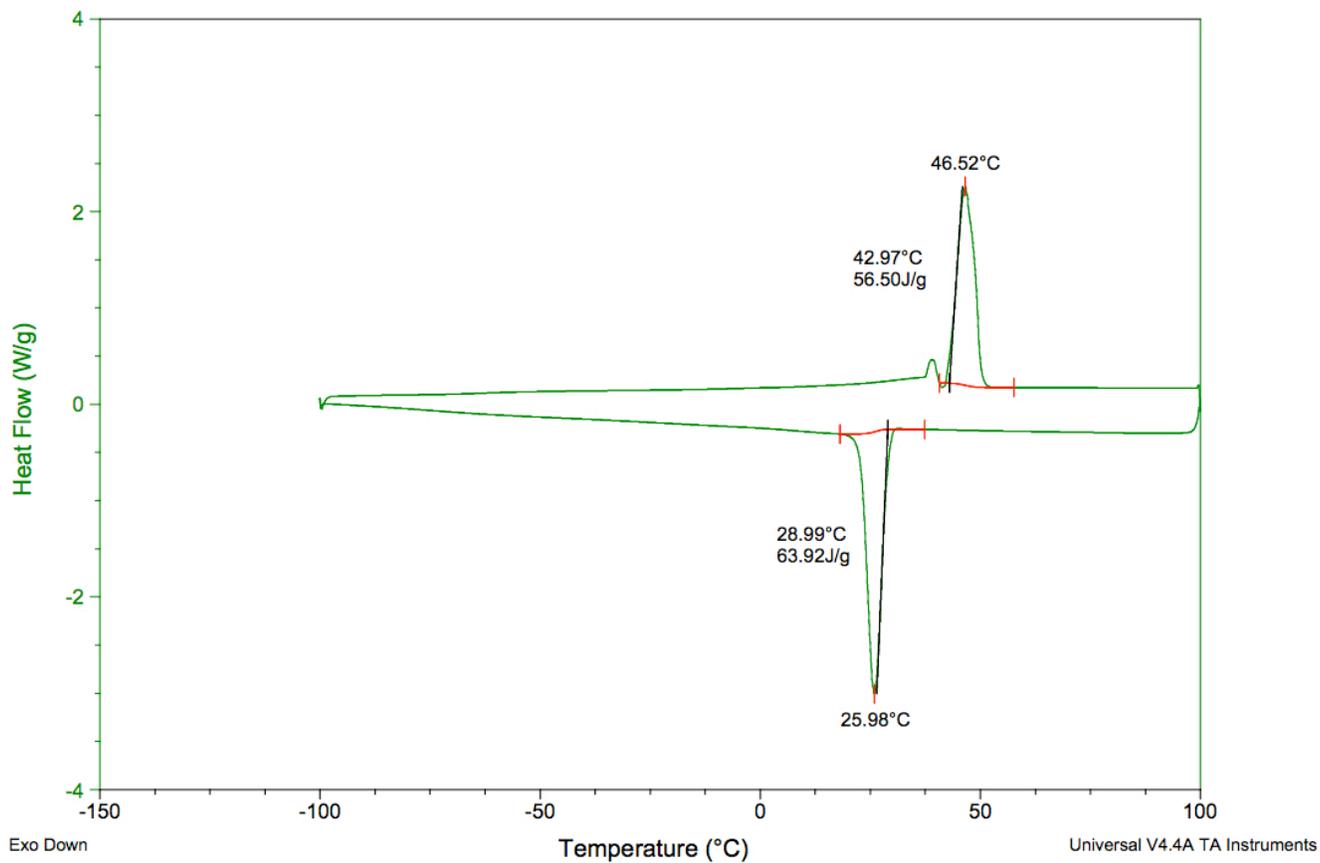


Figure S55. DSC Thermogram of polyoctylene acetal (Table S1, entry 4).

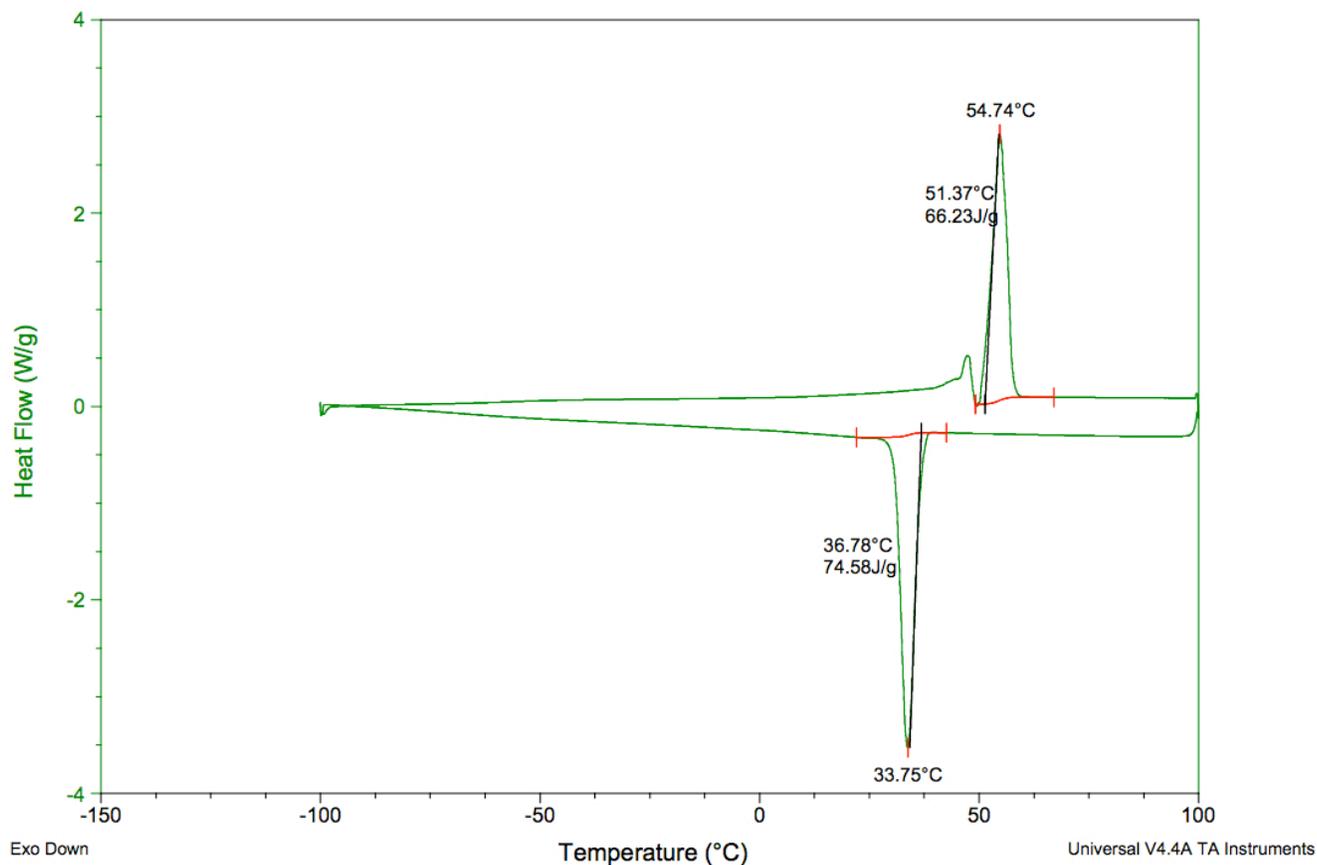


Figure S56. DSC Thermogram of polynonylene acetal (Table S1, entry 5).

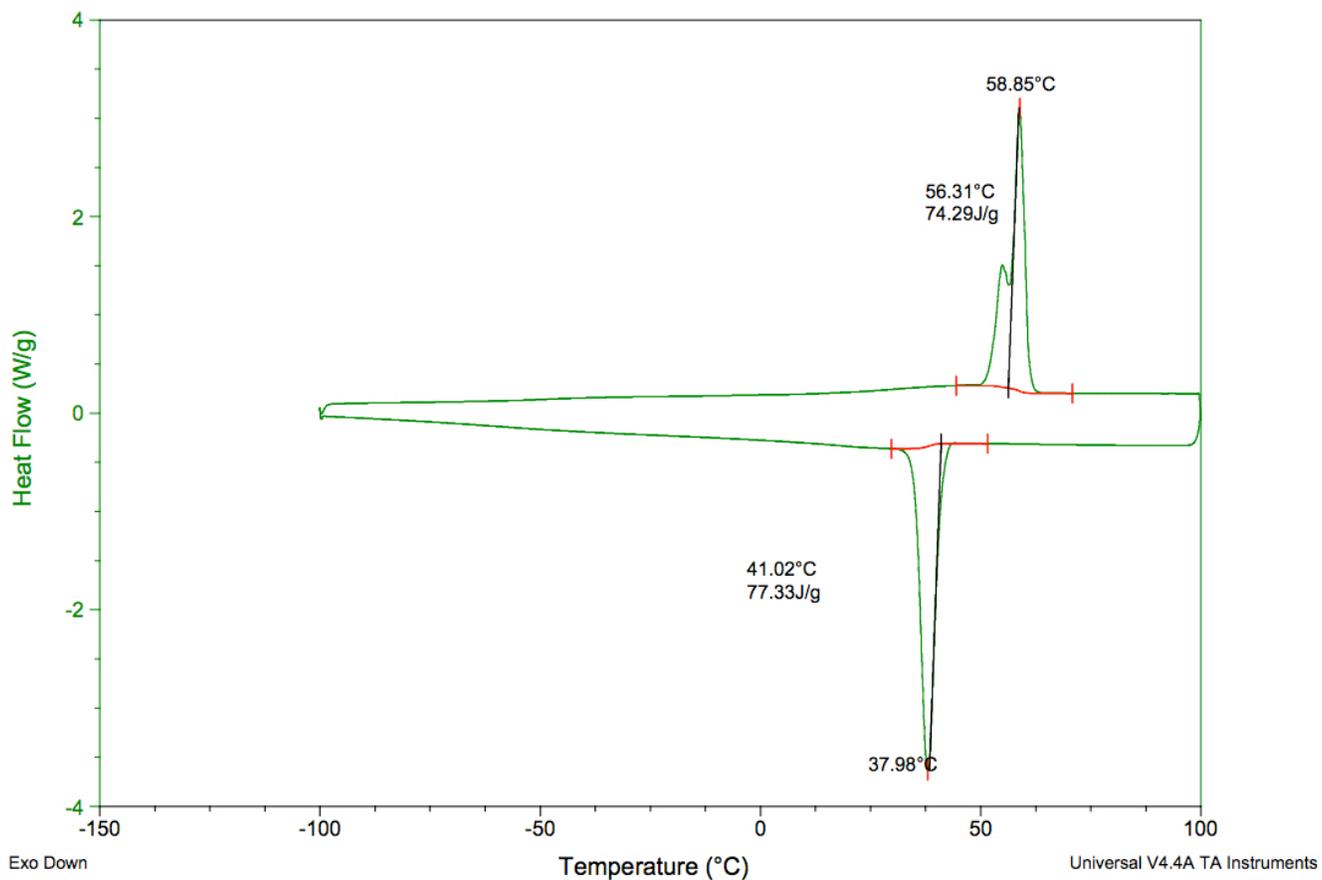


Figure S57. DSC Thermogram of polydecylene acetal (Table S1, entry 6).

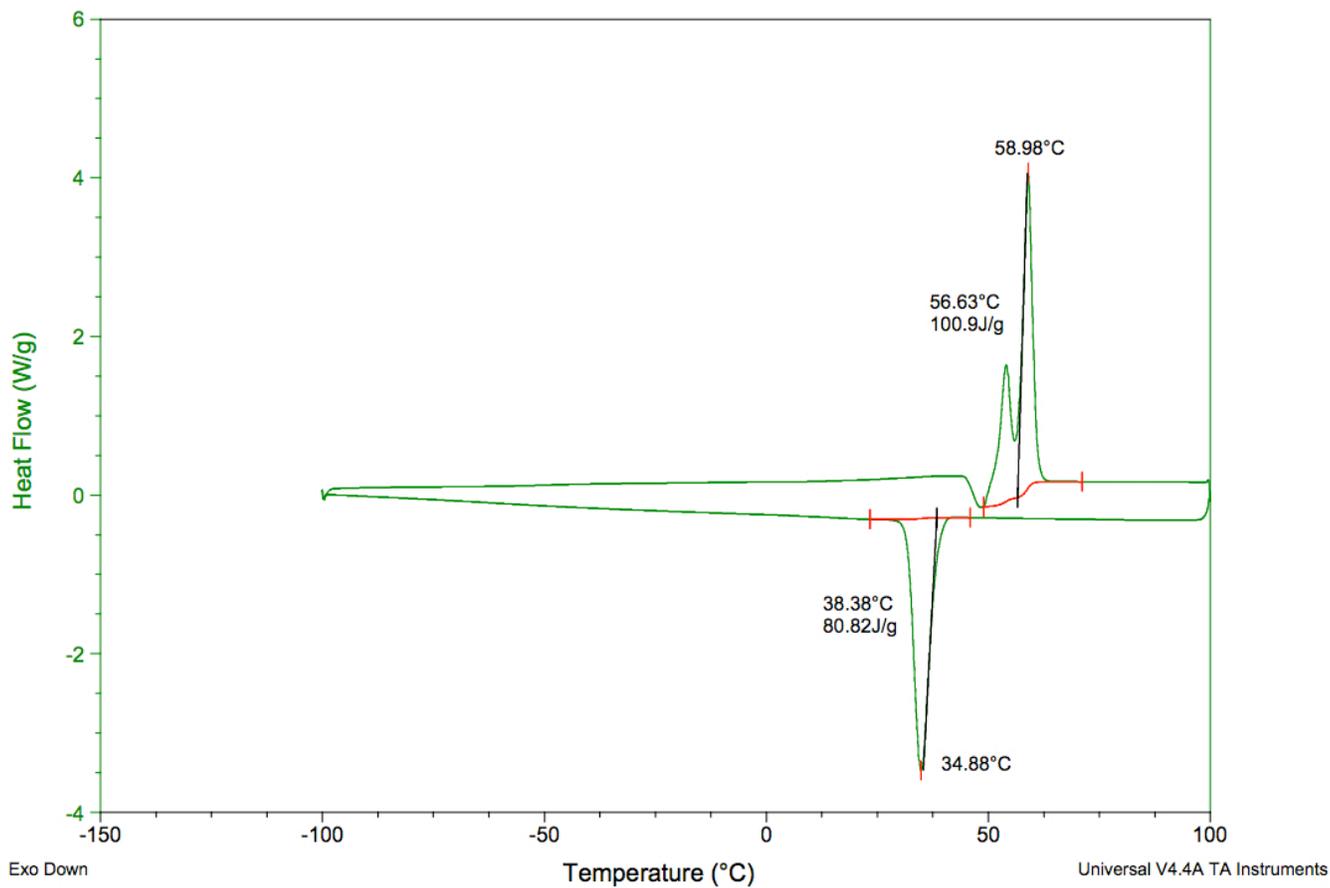


Figure S58. DSC Thermogram of polydecylene acetal, *from the two-pot synthesis* (Table S1, entry 7).

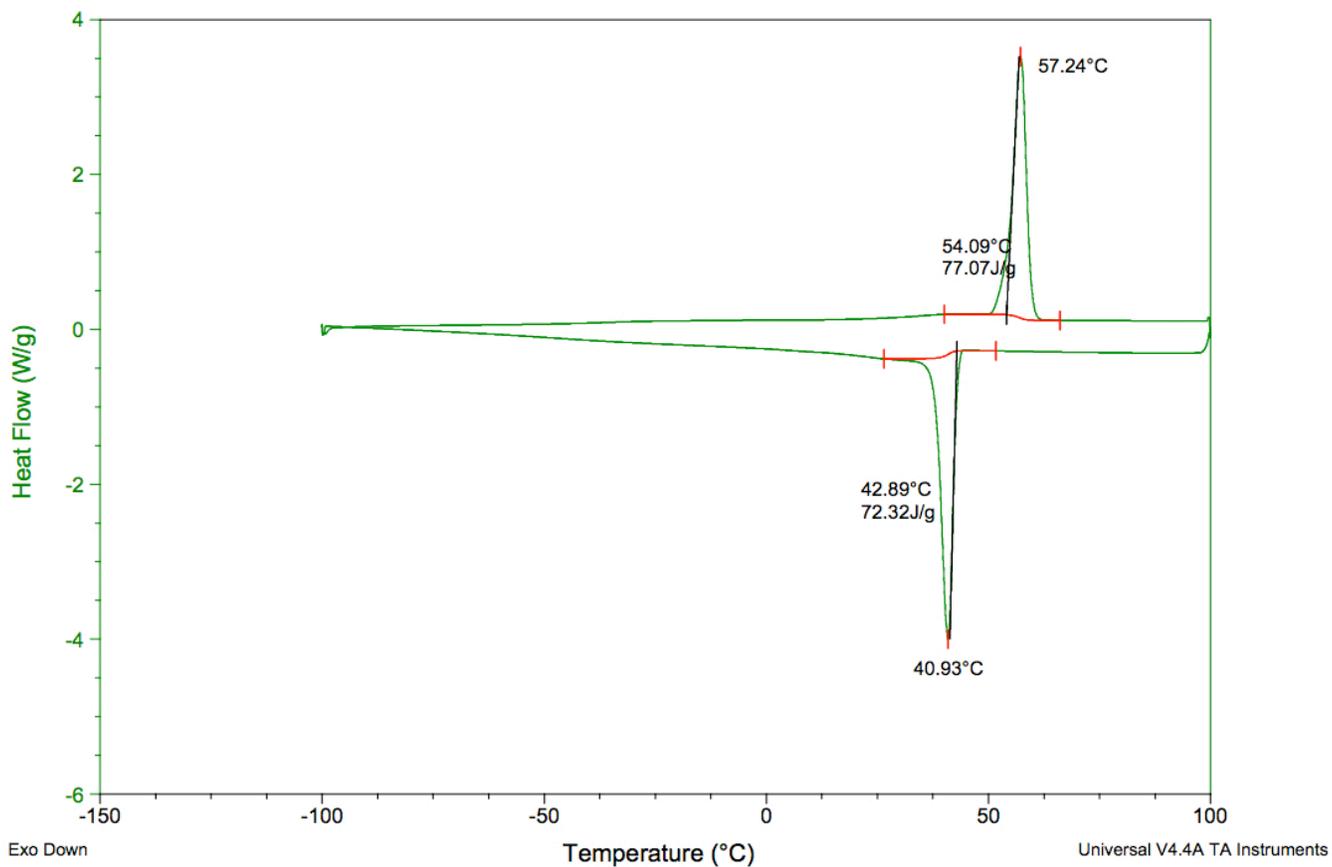


Figure S59. DSC Thermogram of polyundecylene acetal (Table S1, entry 8).

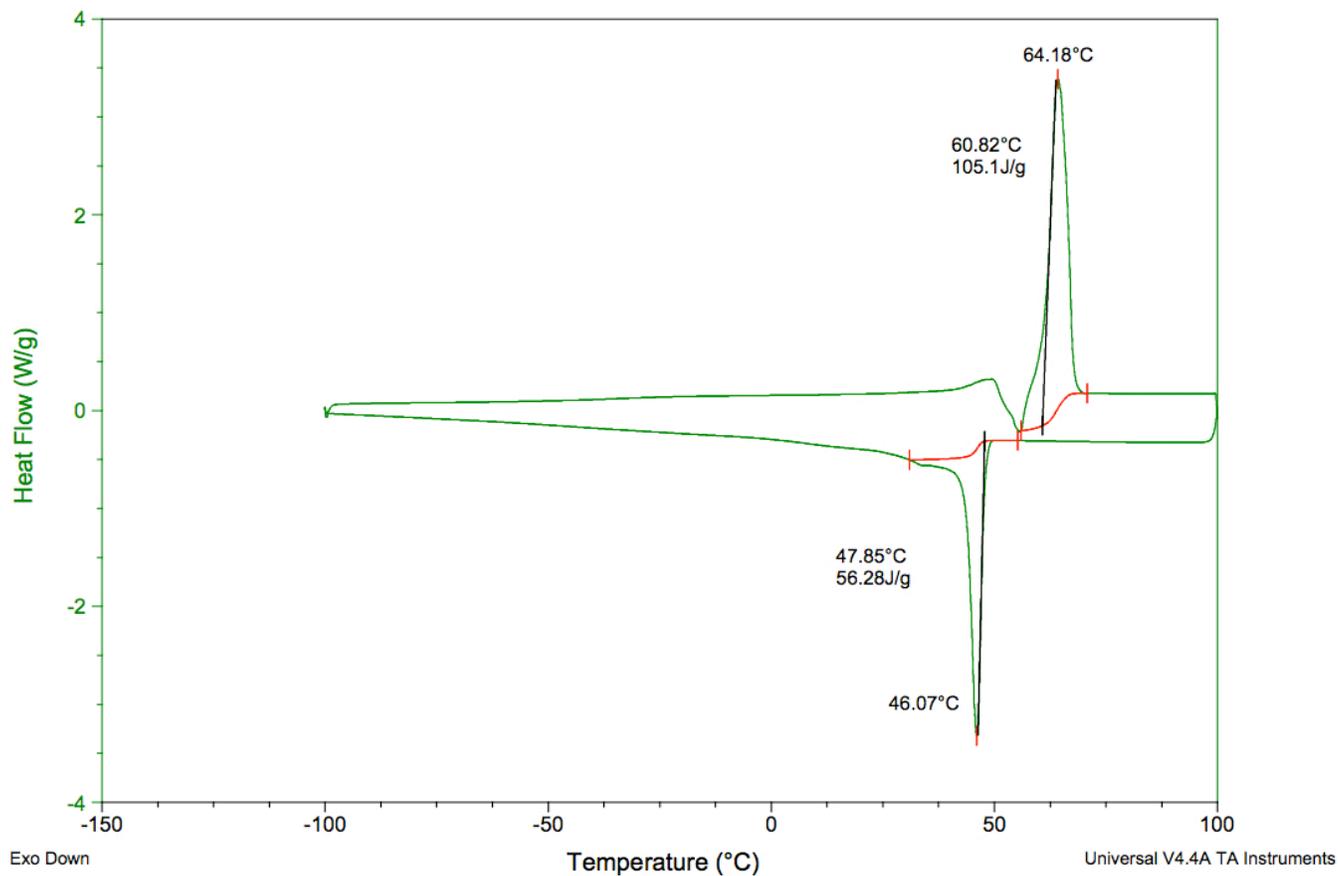


Figure S60. DSC Thermogram of polydodecylene acetal (Table S1, entry 9).

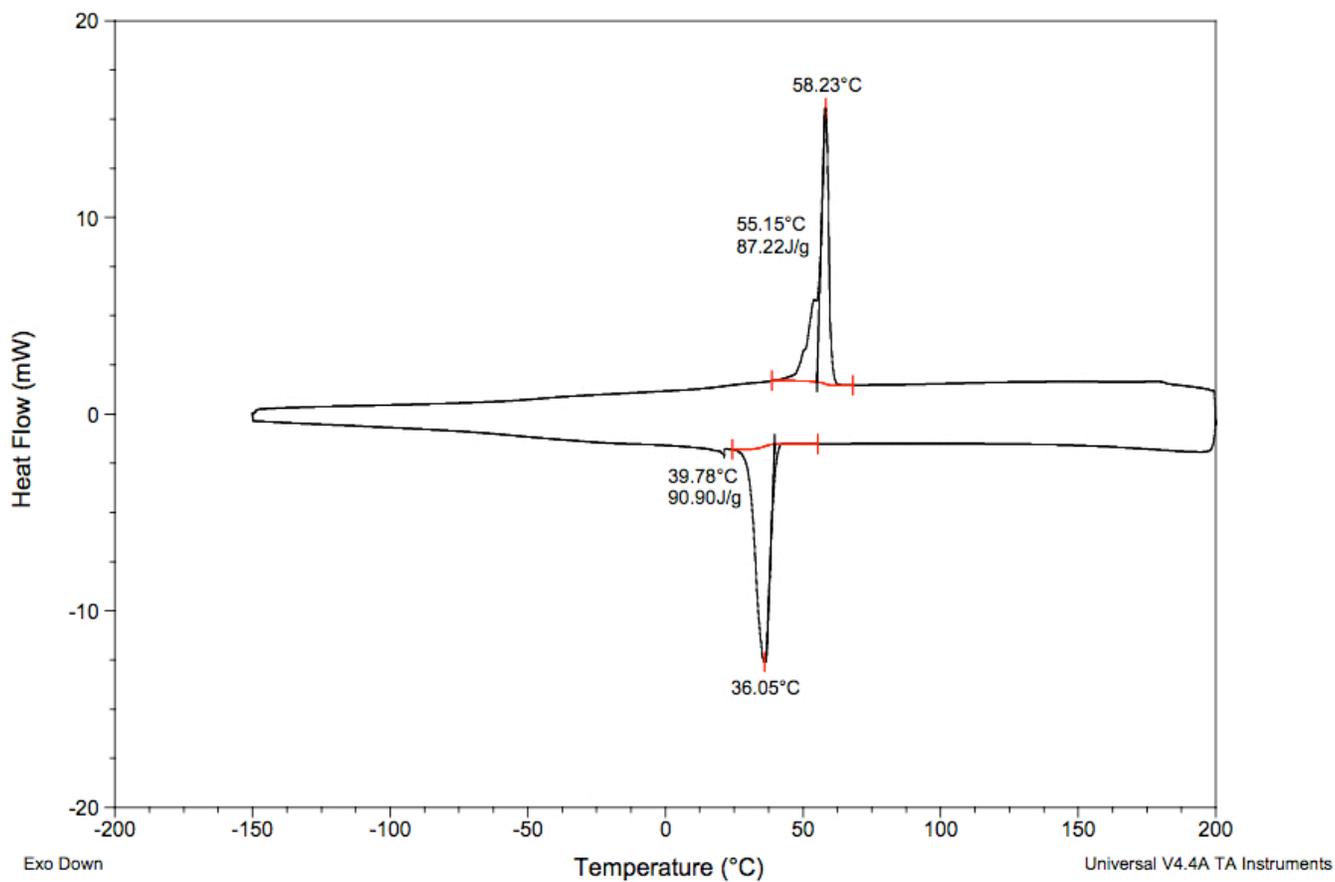


Figure S61. DSC Thermogram of polydecylene acetal, 10 gram scale-up (Table S1, entry 10).

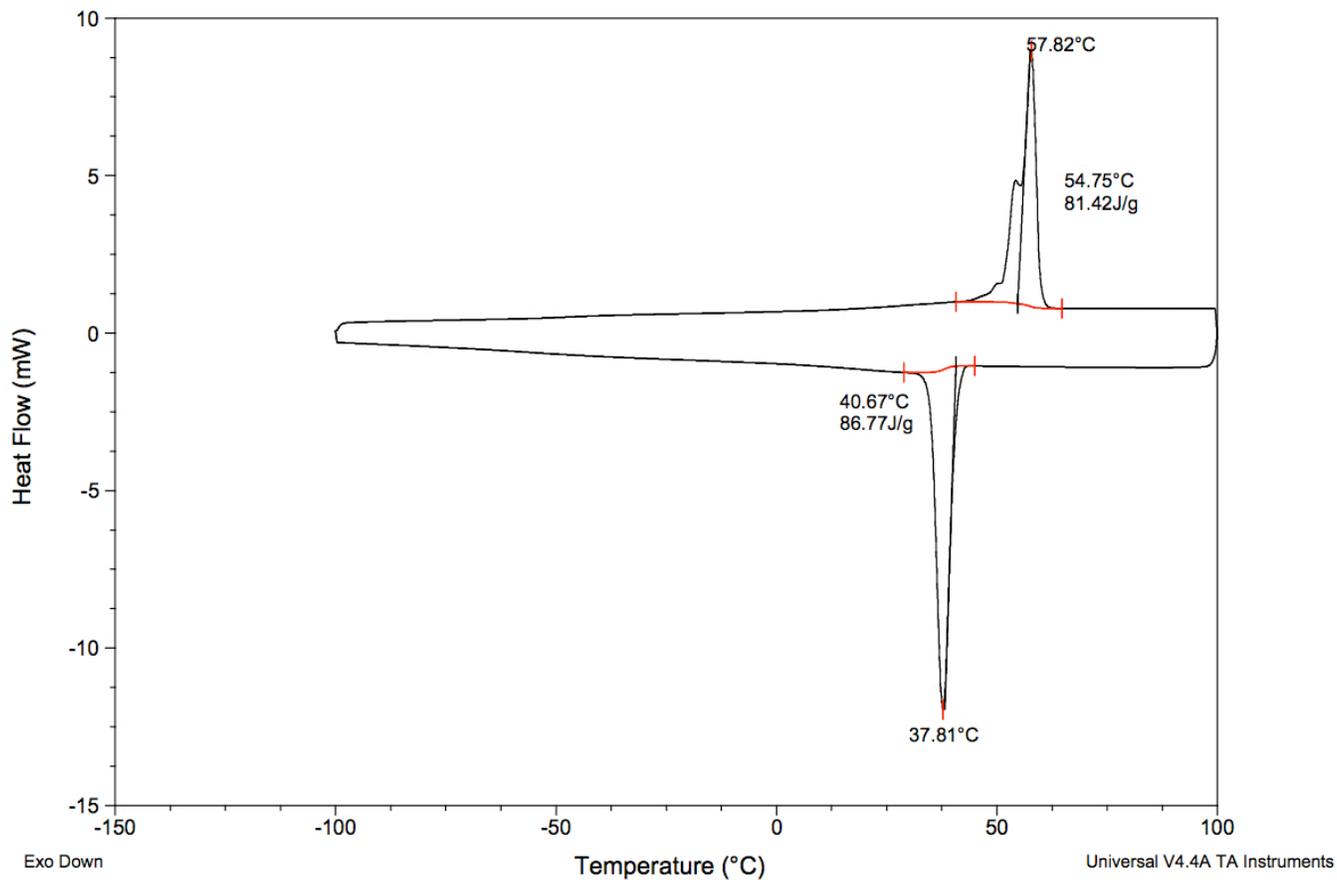


Figure S62. DSC Thermogram of polydecylene acetal, 50 gram scale-up (Table S1, entry 11).

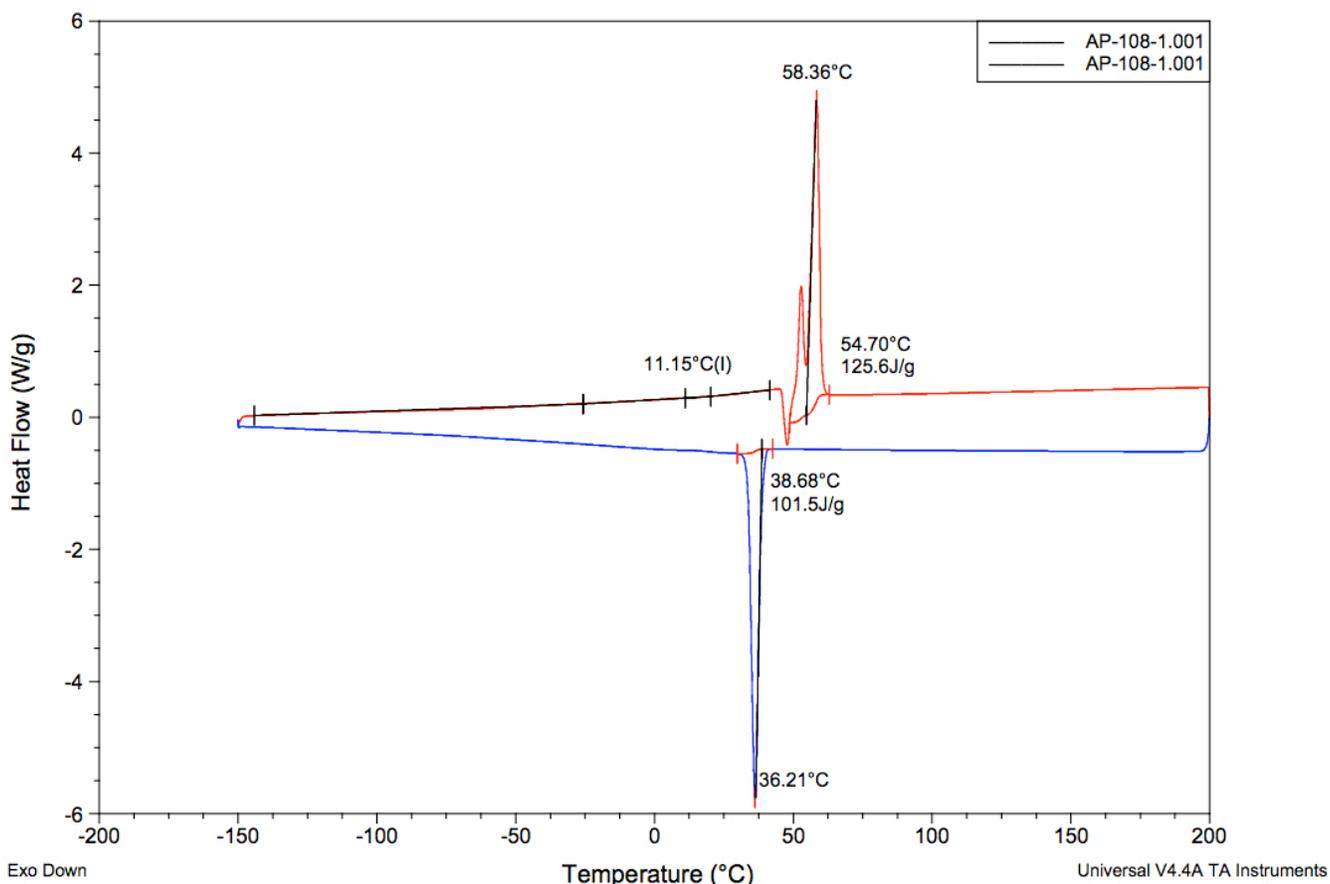


Figure S63. DSC Thermogram of polydecylene acetal, first iteration (Table S1, entry 12).

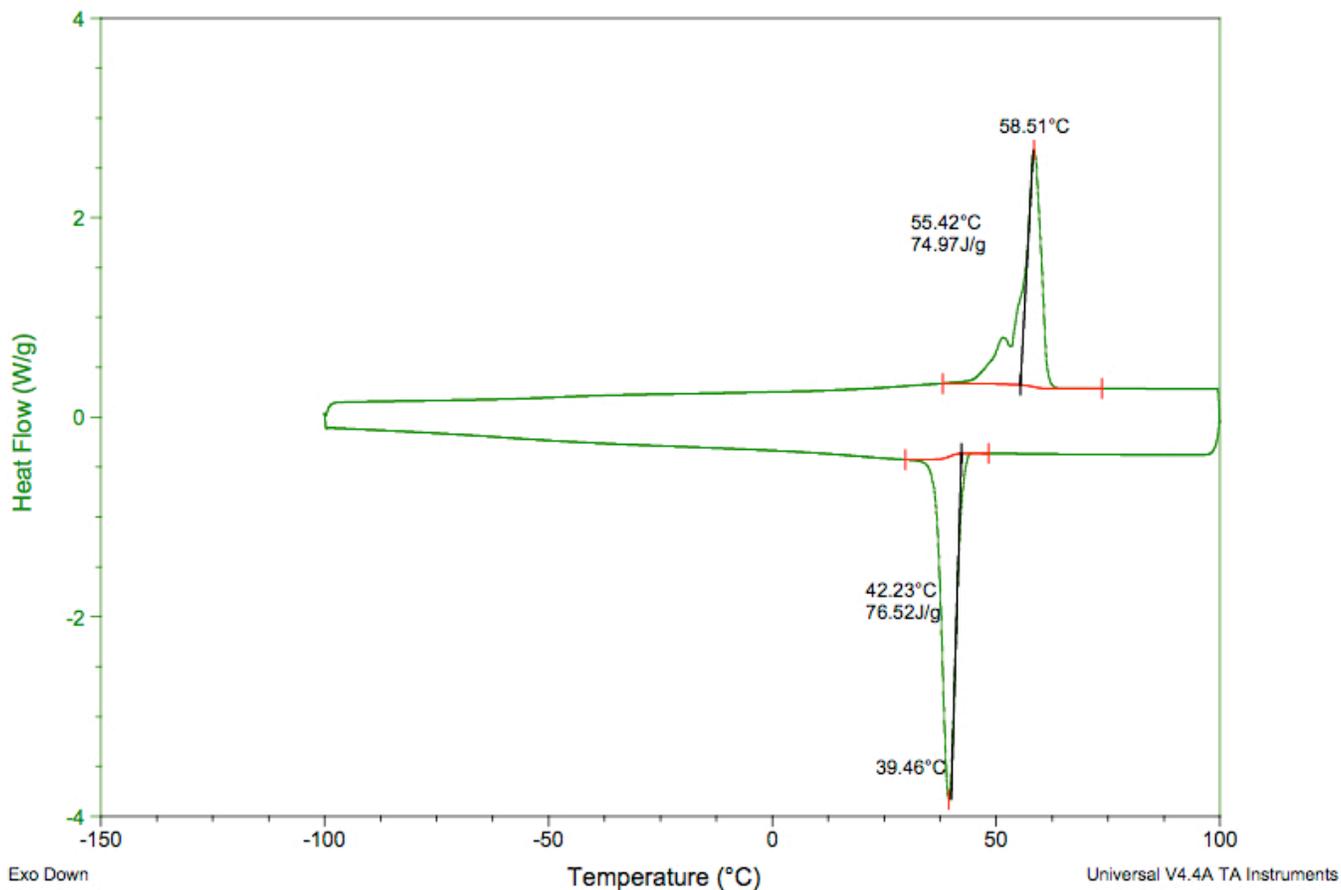


Figure S64. DSC Thermogram of polydecylene acetal, *second iteration* (Table S1, entry 13).

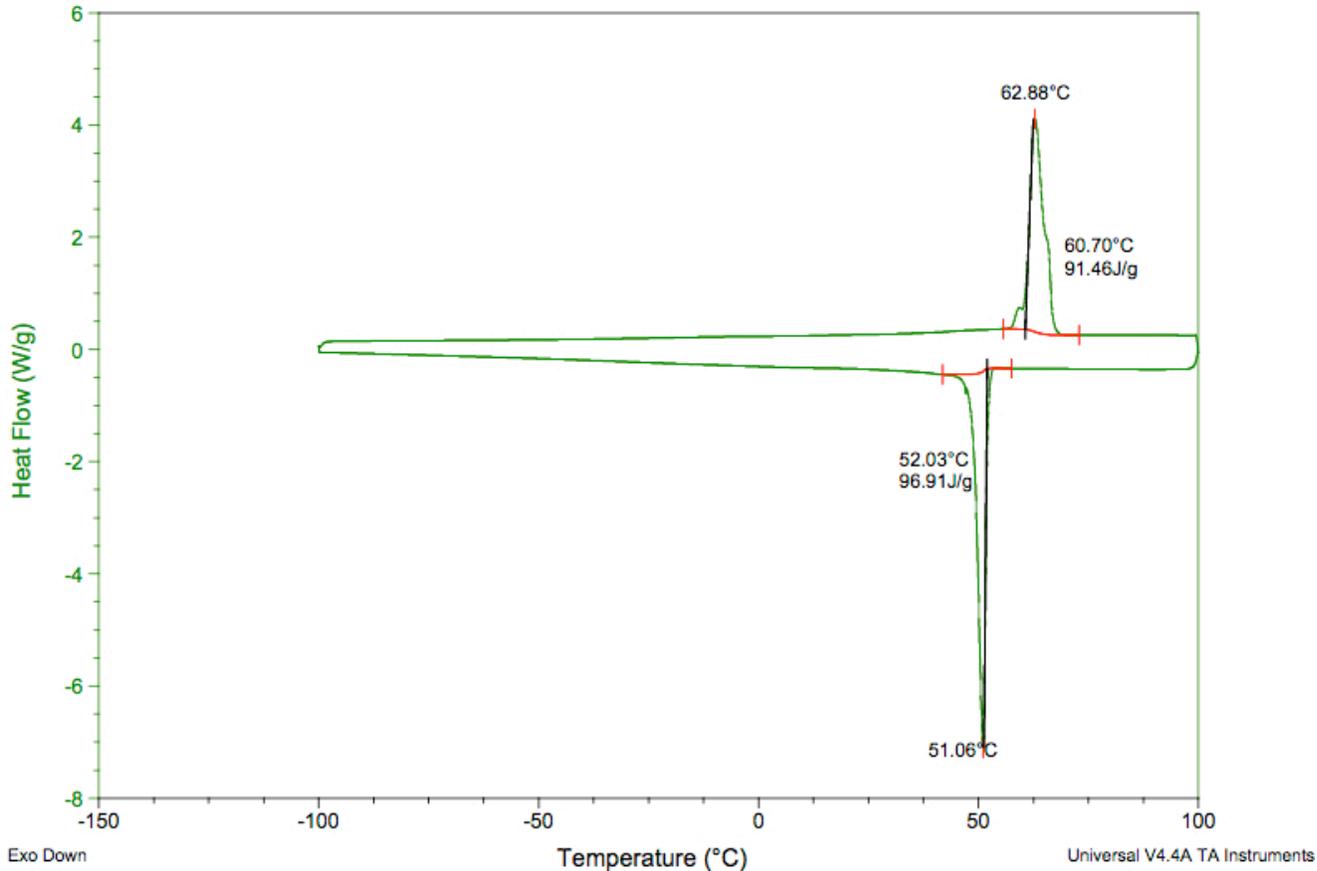


Figure S65. DSC Thermogram of polydodecylene acetal, *first iteration* (Table S1, entry 14).

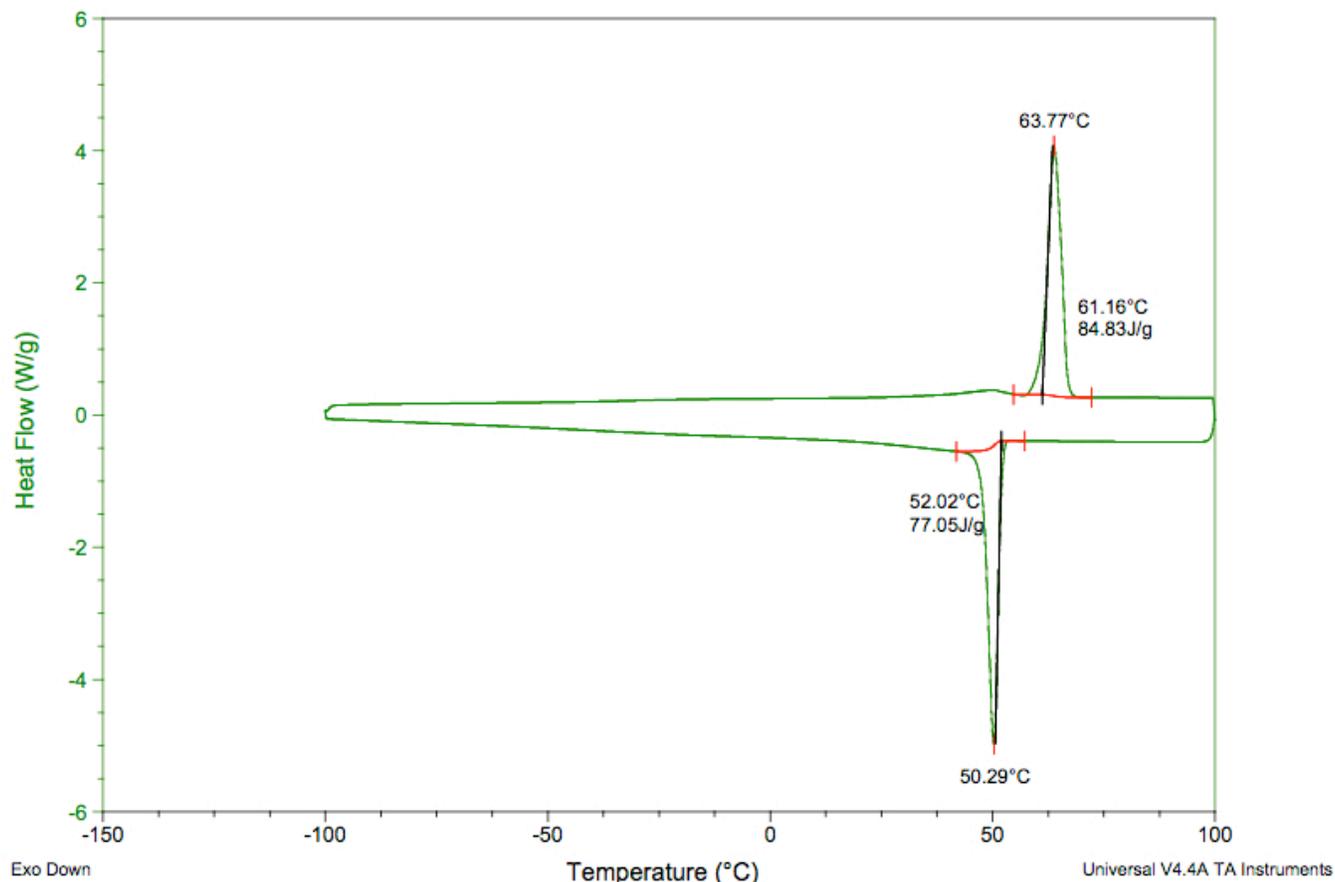


Figure S66. DSC Thermogram of polydodecylene acetal, *second iteration* (Table S1, entry 15).

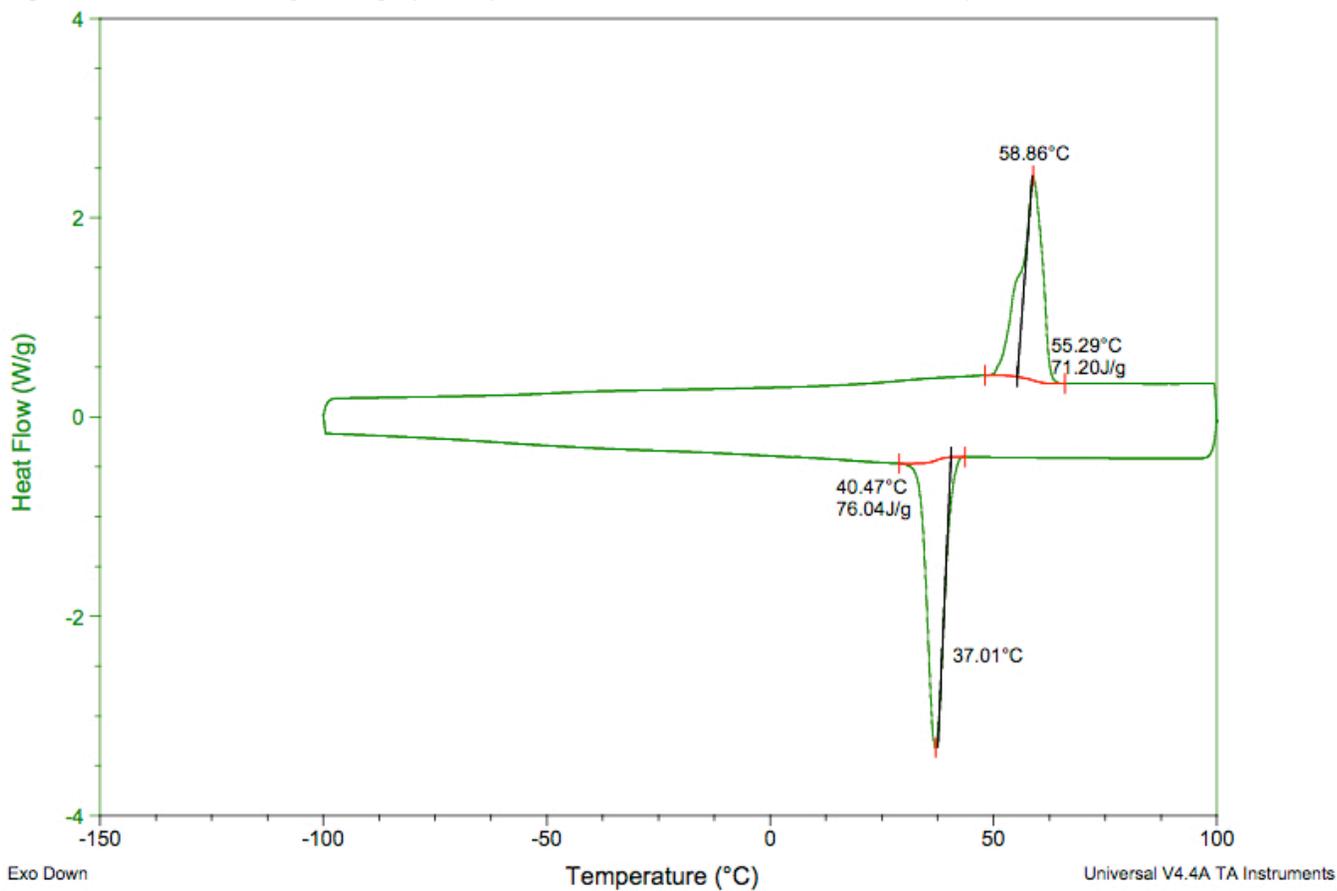


Figure S67. DSC Thermogram of polydecylene acetal, *from dimethoxymethane* (Table S1, entry 16).

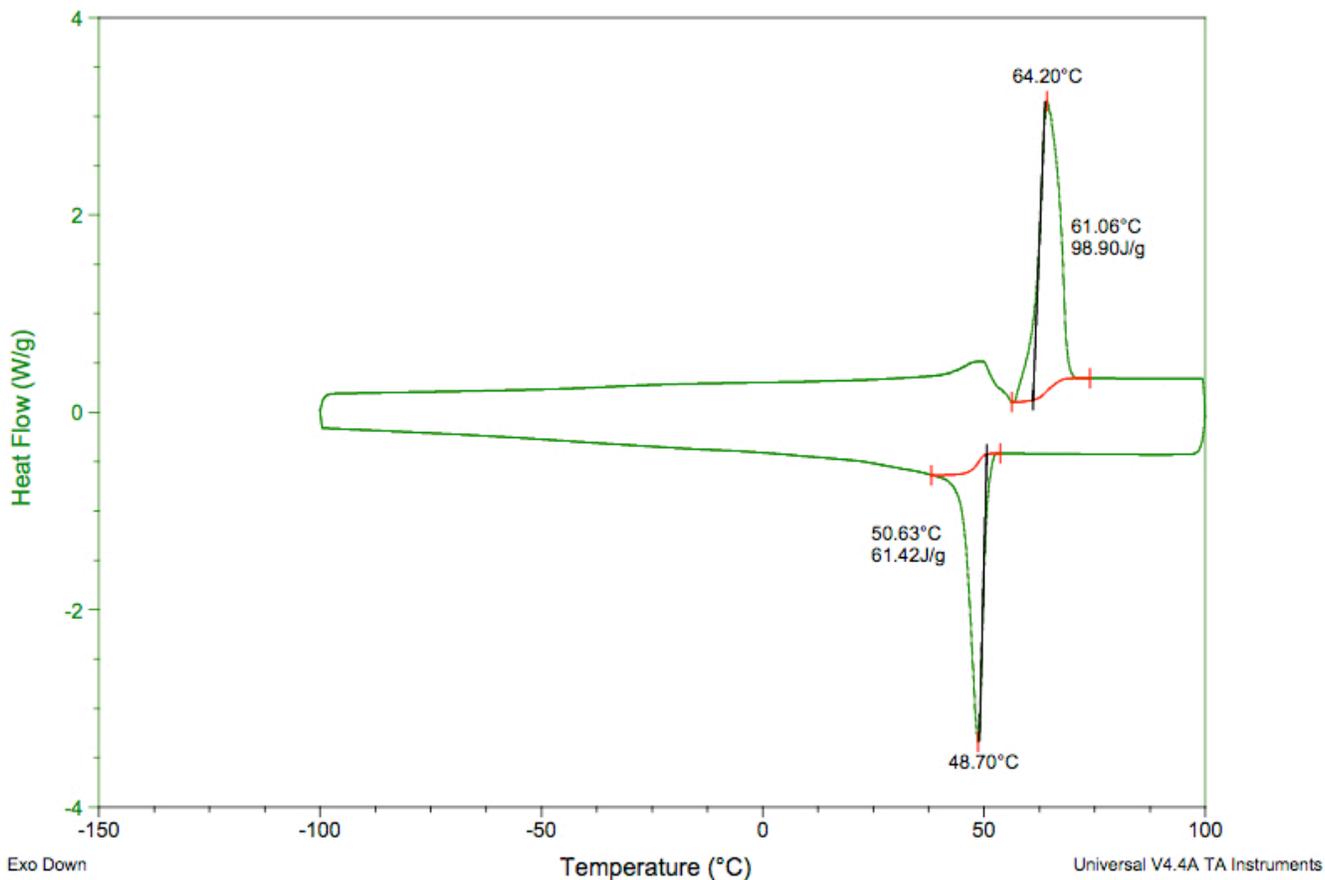


Figure S68. DSC Thermogram of polydodecylene acetal, *from dimethoxymethane* (Table S1, entry 17).

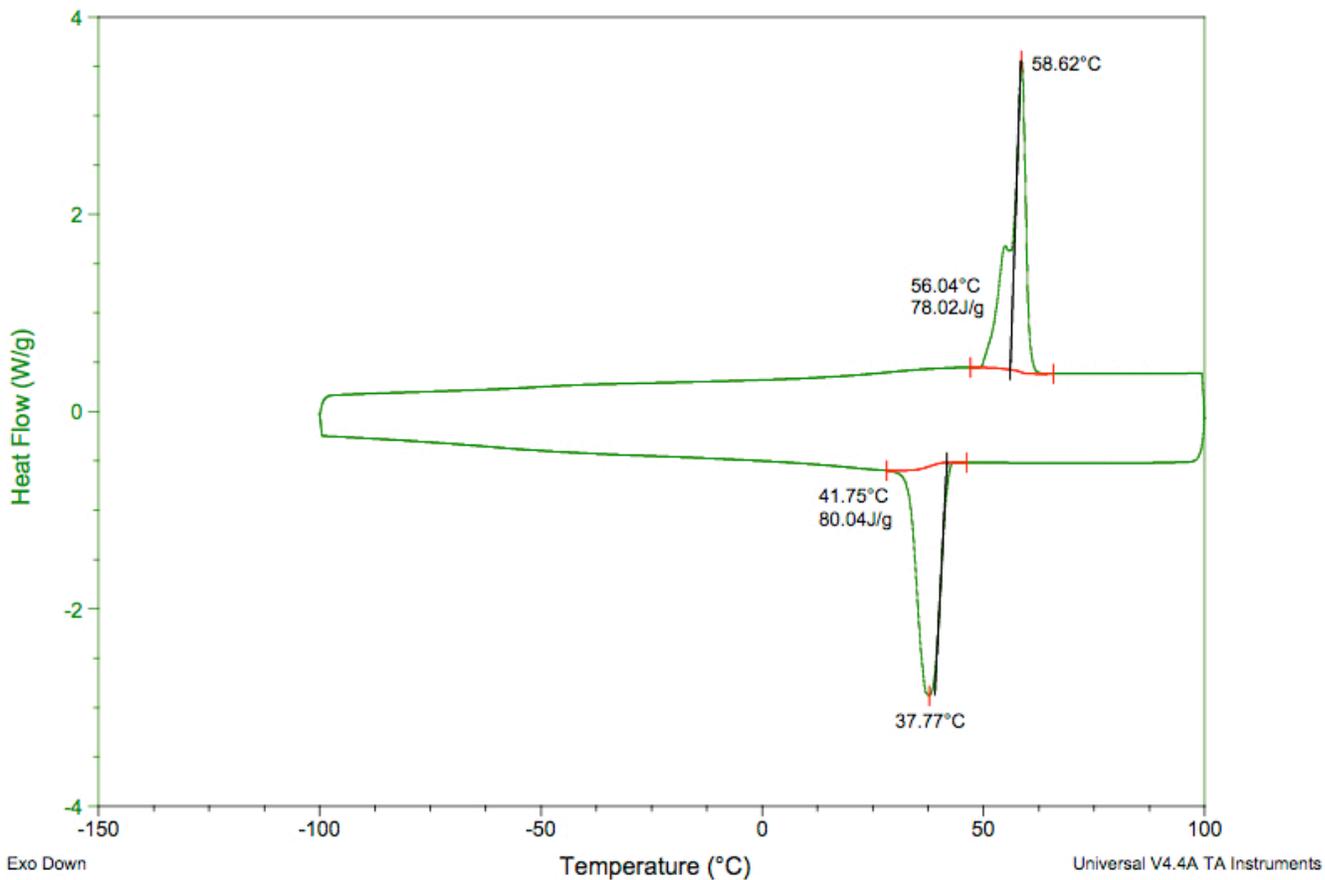


Figure S69. DSC Thermogram of polydecylene acetal, *from diethoxymethane:diol = 2:1* (Table S1, entry 18).

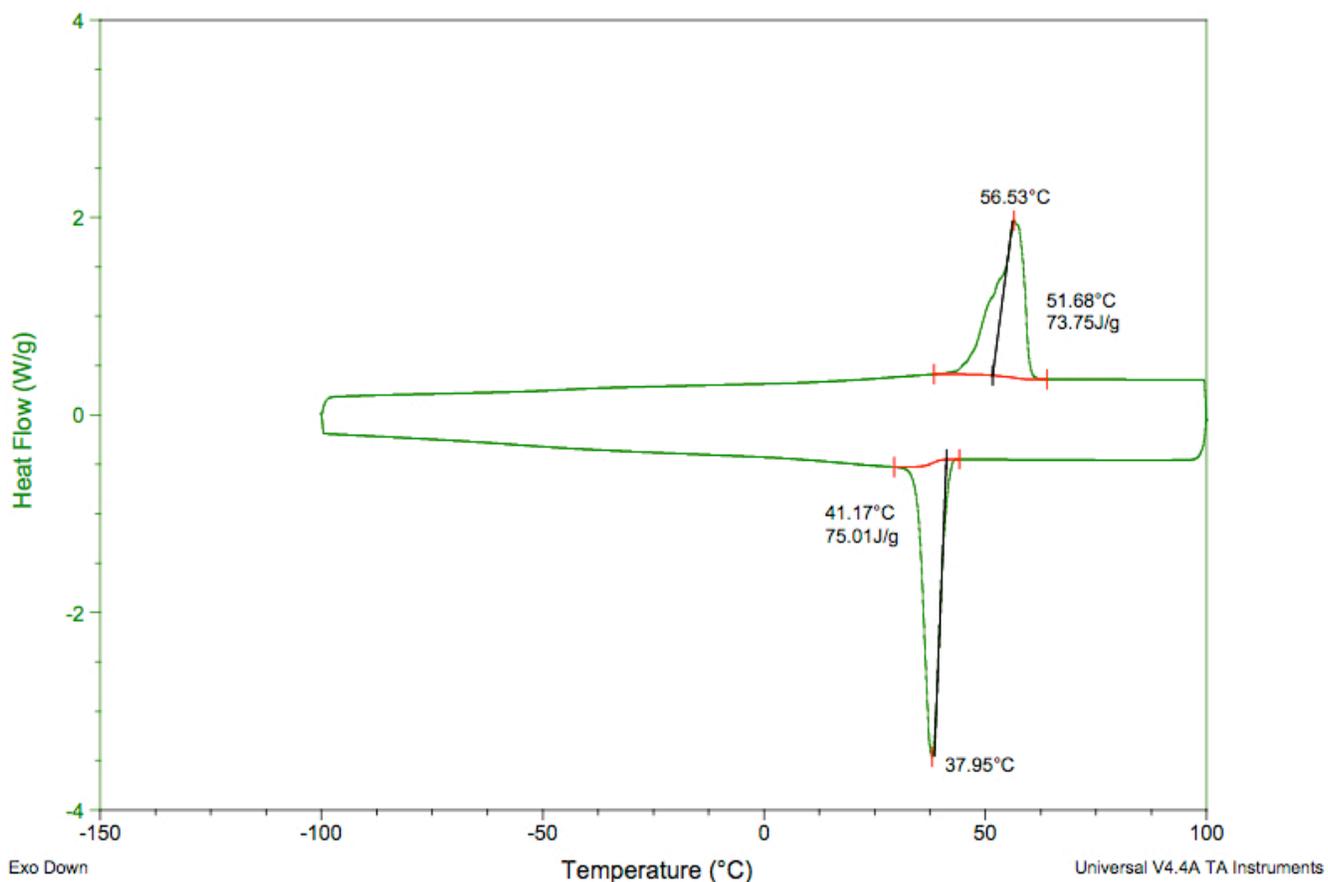


Figure S70. DSC Thermogram of polydecylene acetal, from dimethoxymethane:diol = 2:1 (Table S1, entry 19).

Thermogravimetric Analysis (TGA) Thermograms

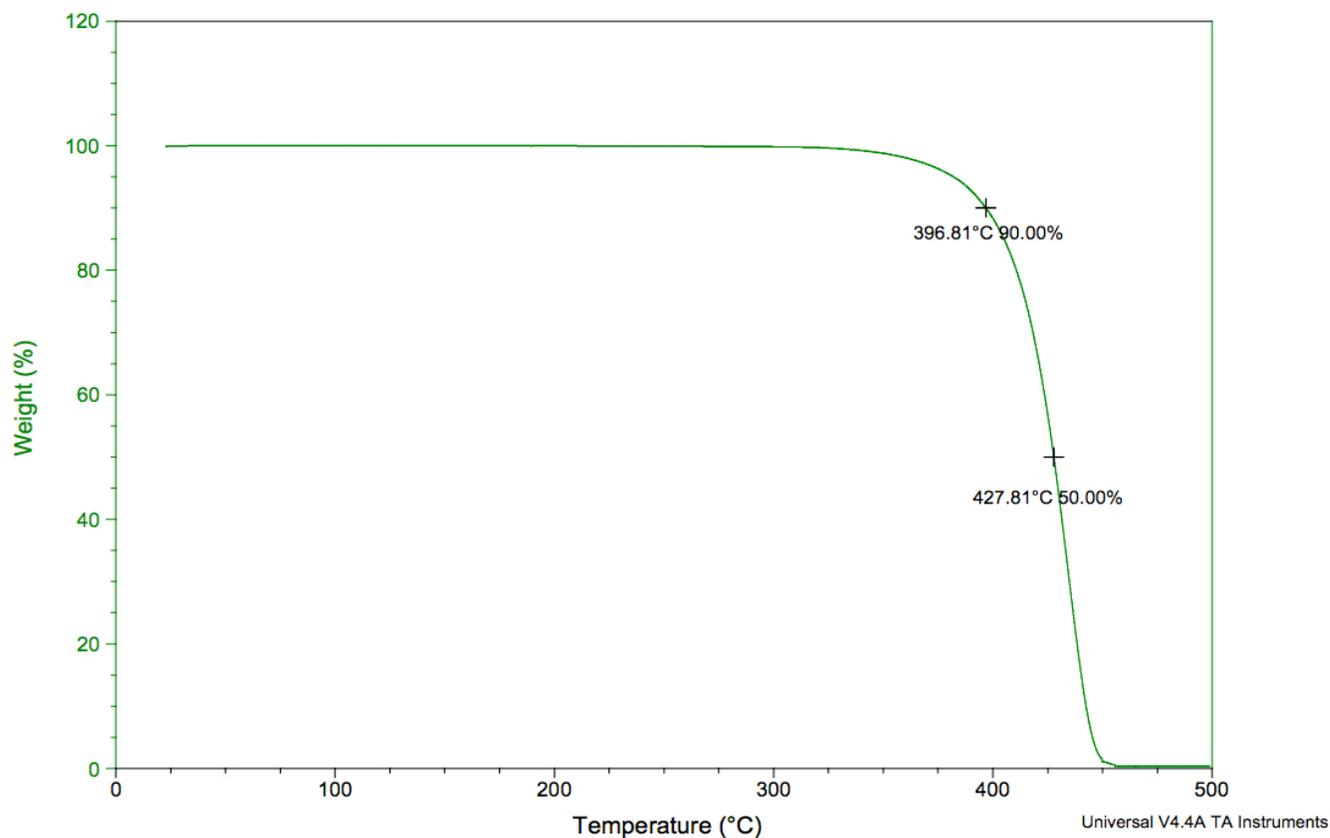


Figure S71. TGA Thermogram of polypentylene acetal (Table S1, entry 1).

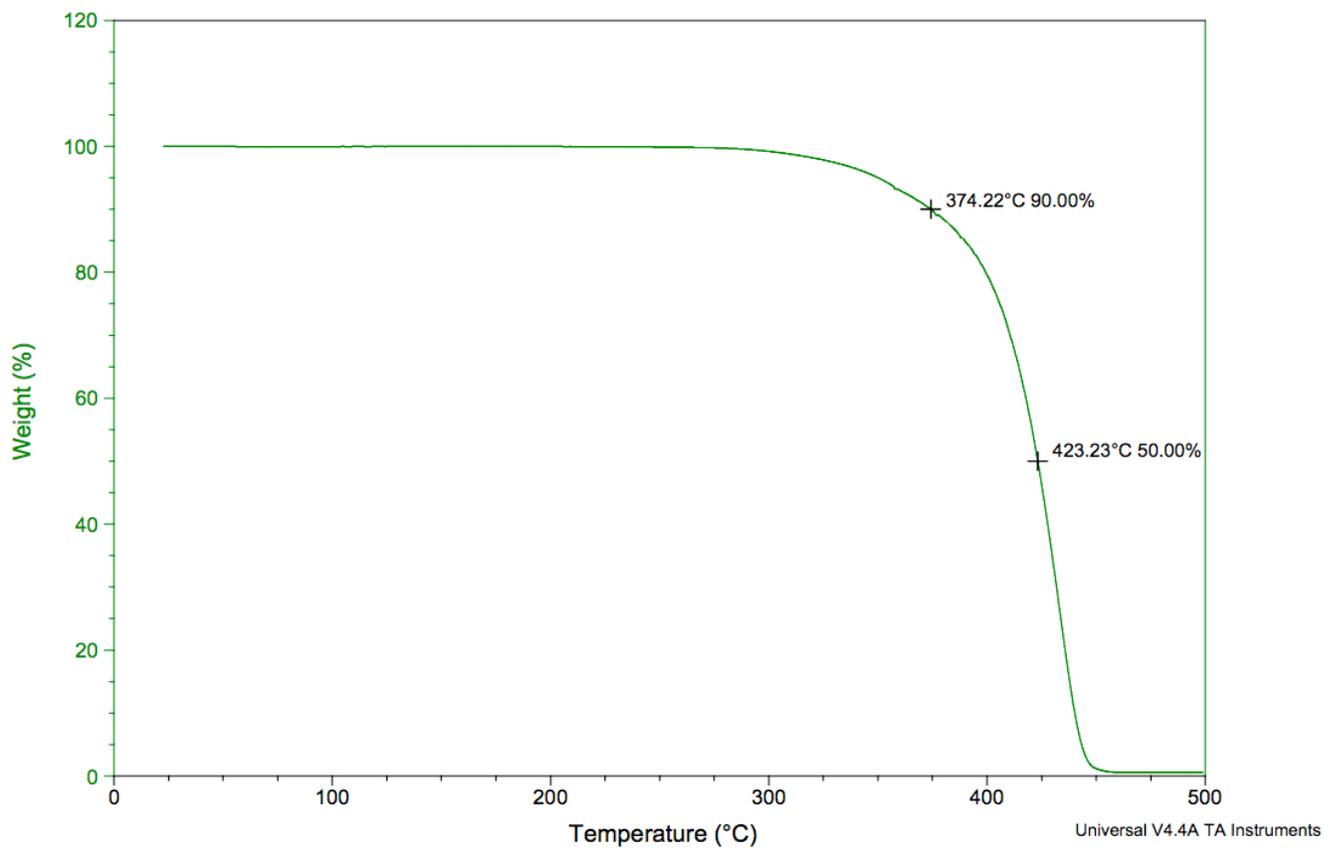


Figure S72. TGA Thermogram of polyhexylene acetal (Table S1, entry 2).

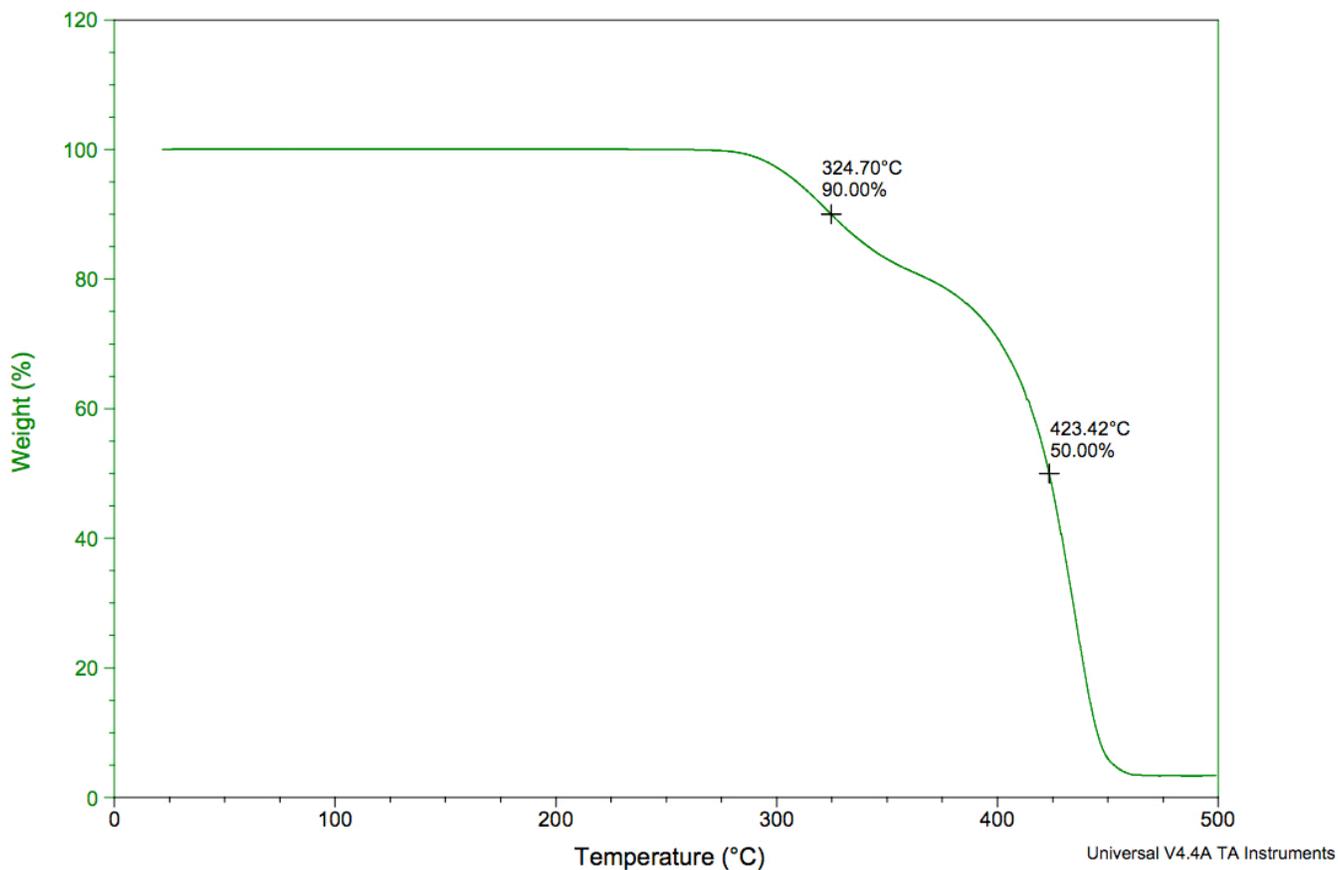


Figure S73. TGA Thermogram of polyheptylene acetal (Table S1, entry 3).

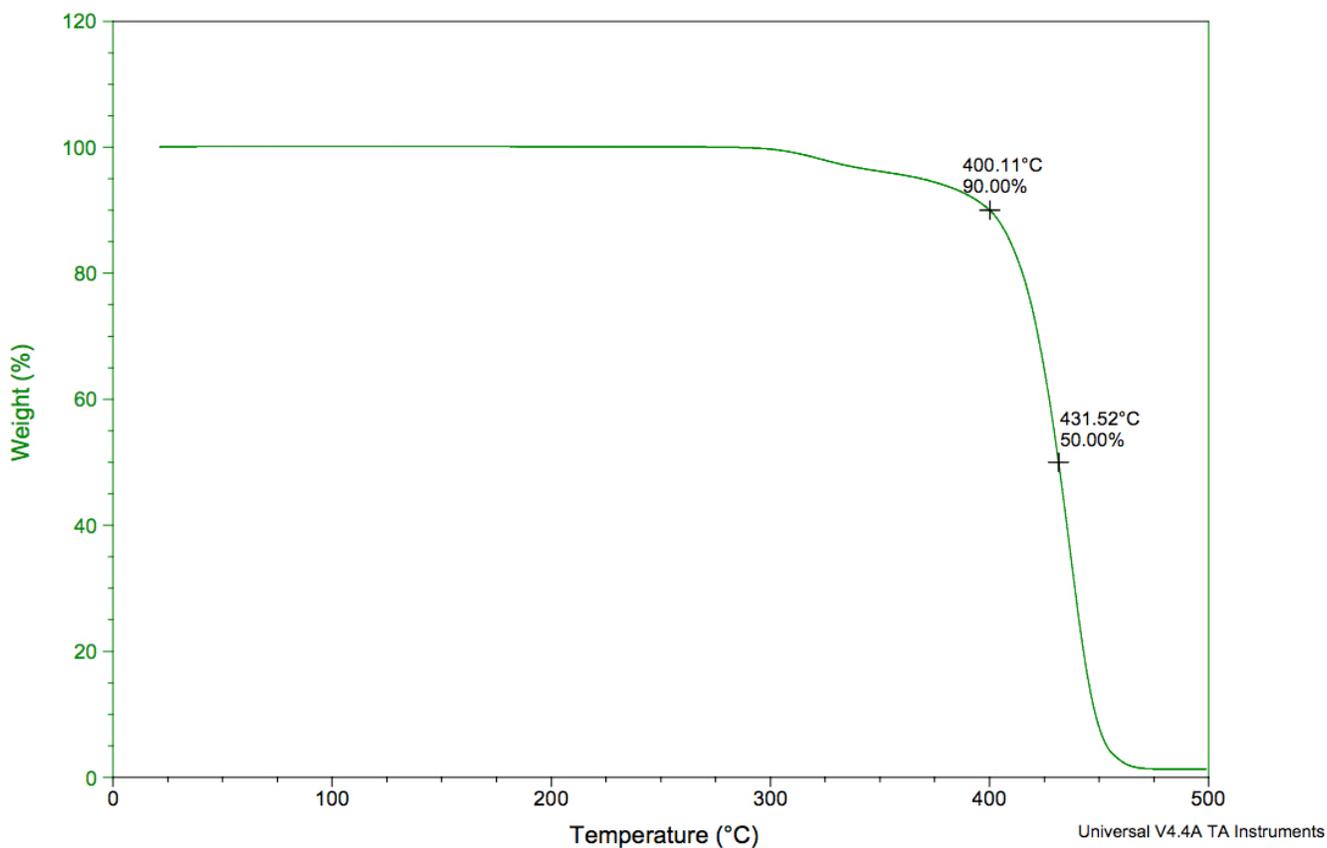


Figure S74. TGA Thermogram of polyoctylene acetal (Table S1, entry 4).

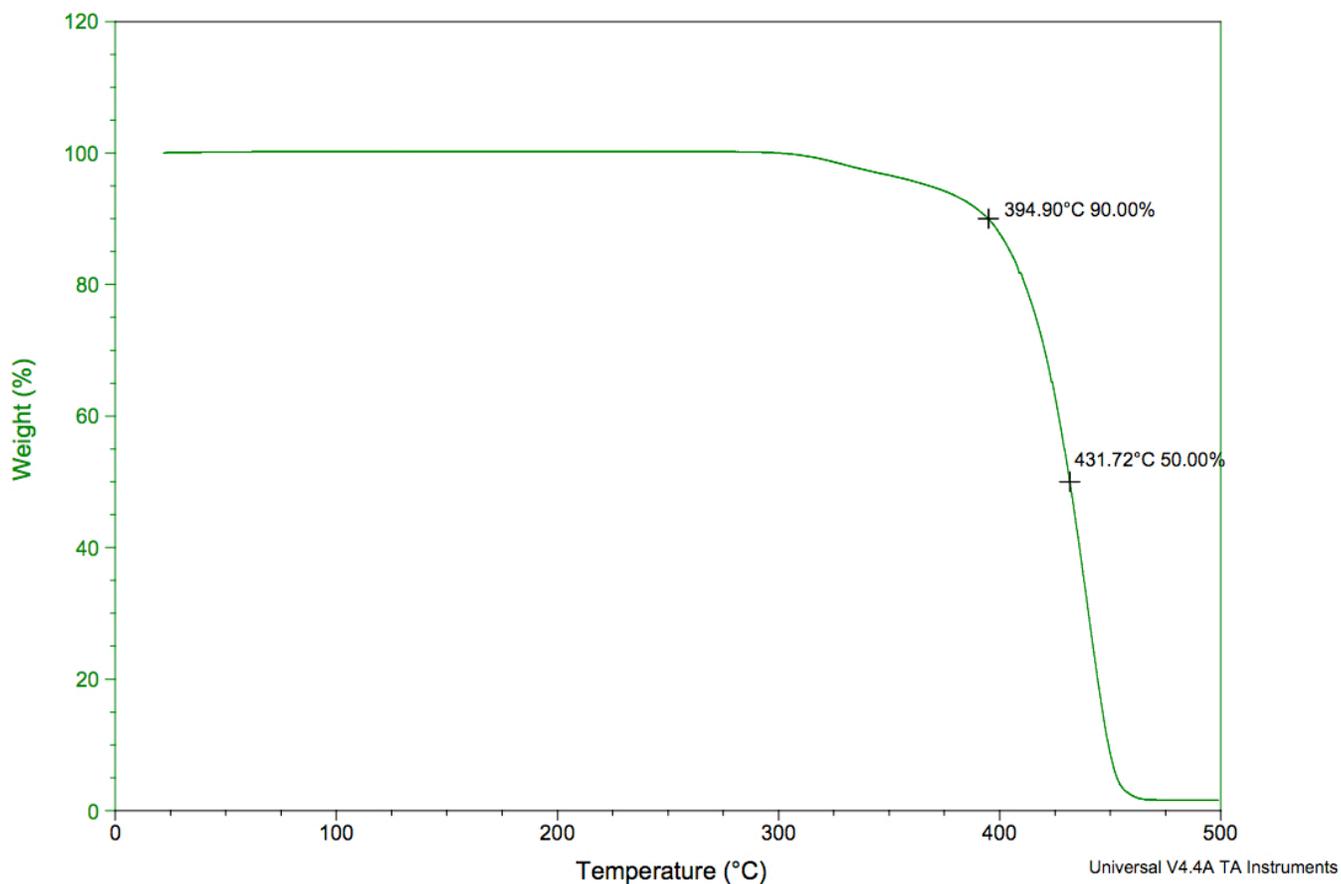


Figure S75. TGA Thermogram of polynonylene acetal (Table S1, entry 5).

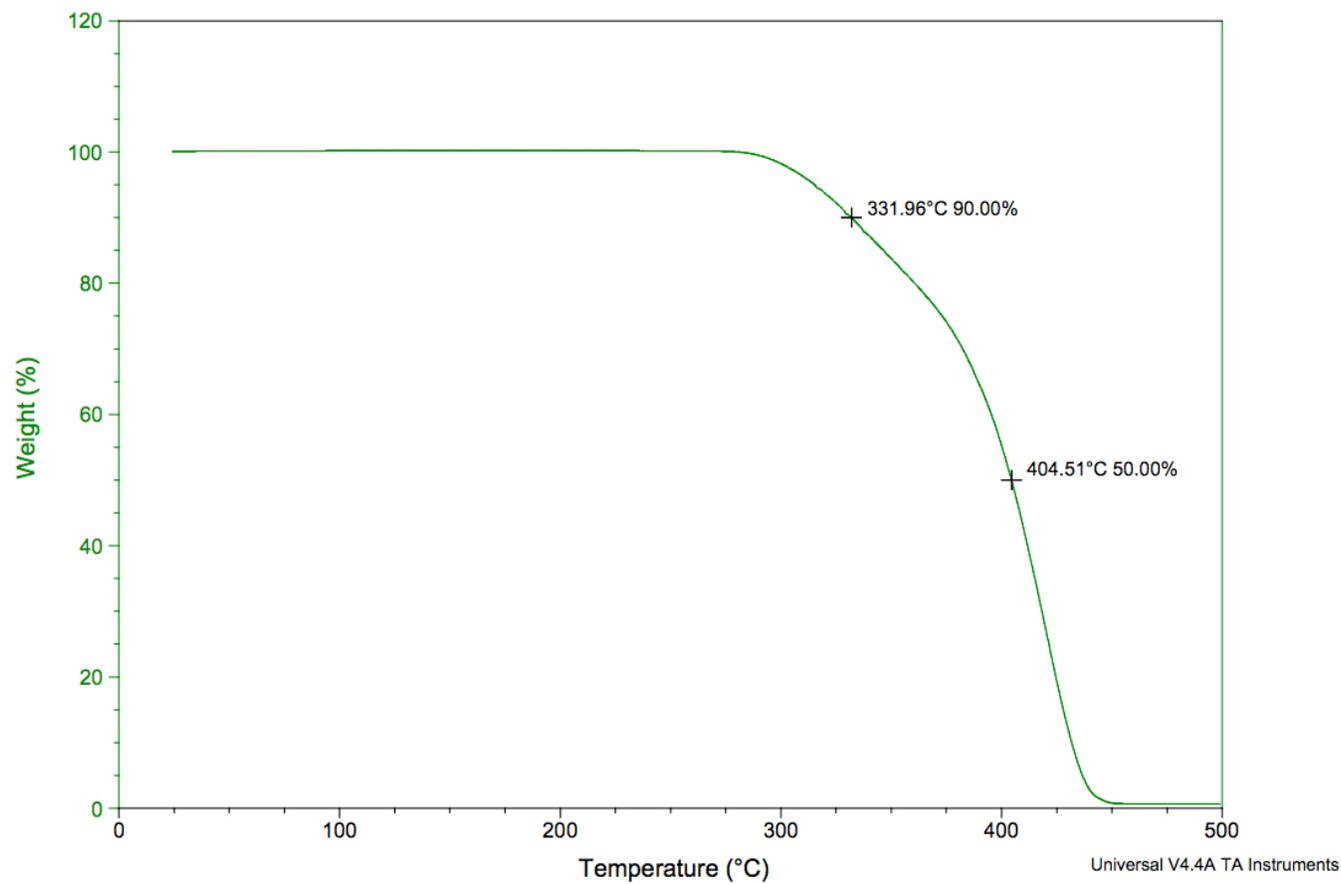


Figure S76. TGA Thermogram of polydecylene acetal (Table S1, entry 6).

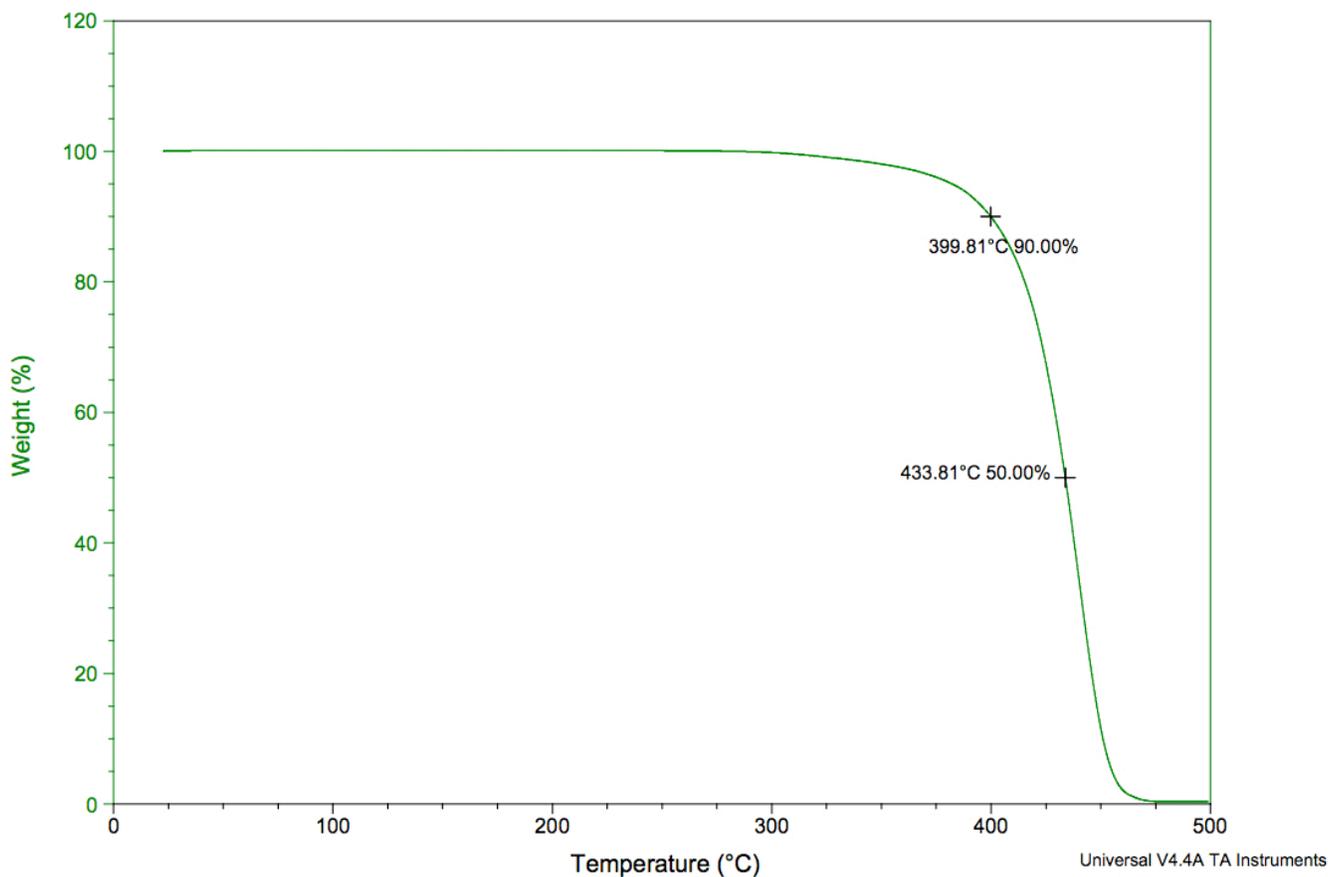


Figure S77. TGA Thermogram of polydecylene acetal, *from the two-pot synthesis* (Table S1, entry 7).

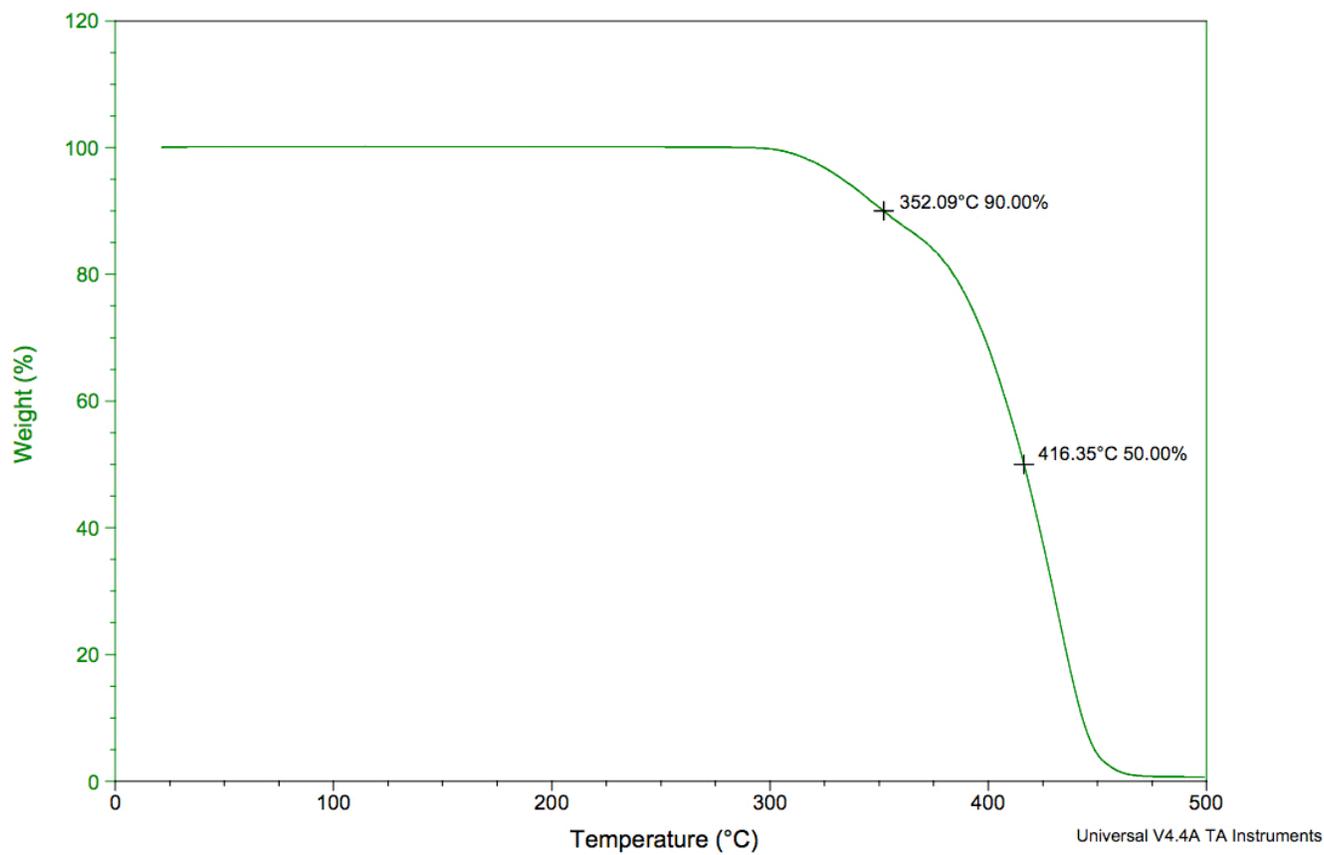


Figure S78. TGA Thermogram of polyundecylene acetal (Table S1, entry 8).

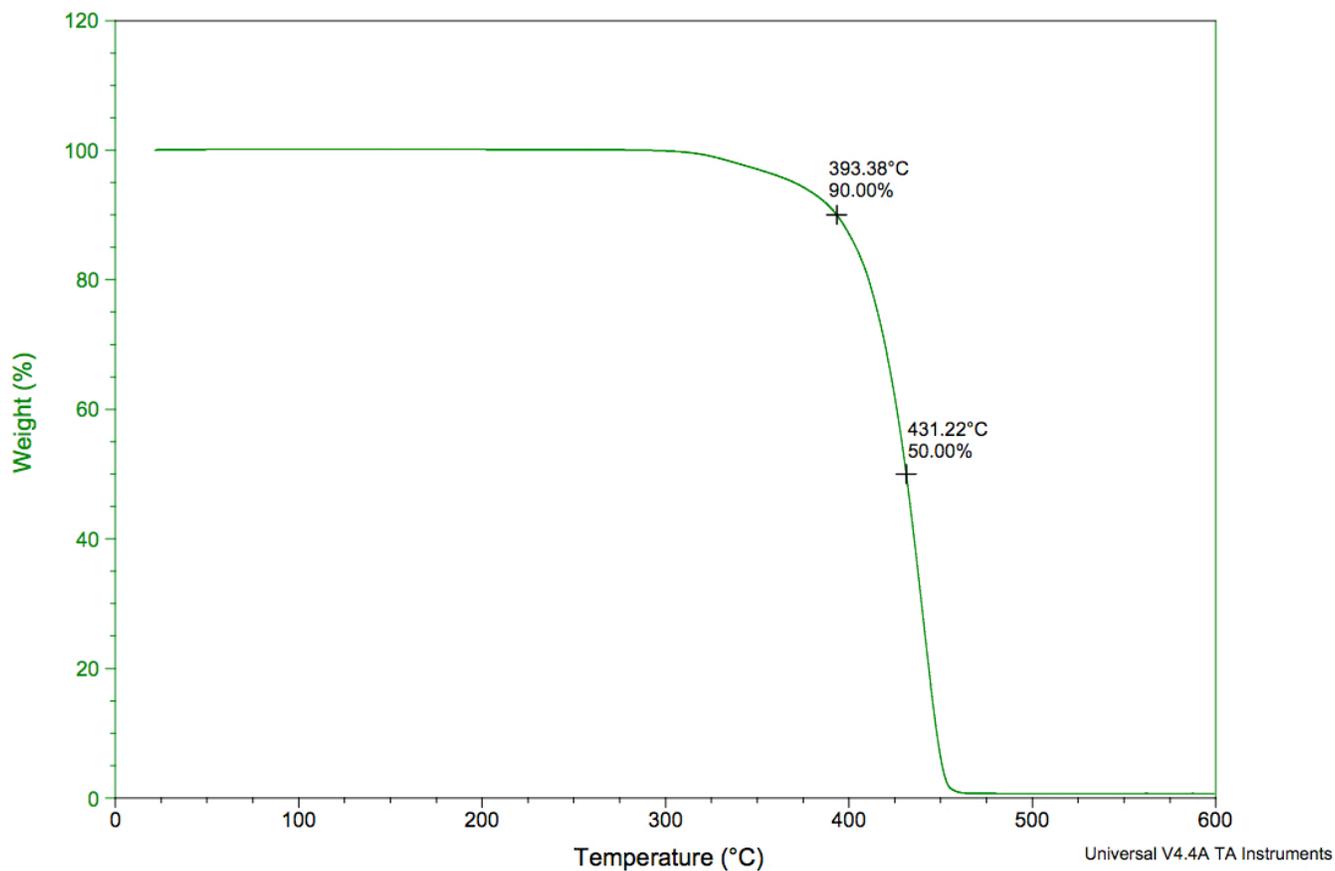


Figure S79. TGA Thermogram of polydodecylene acetal (Table S1, entry 9).

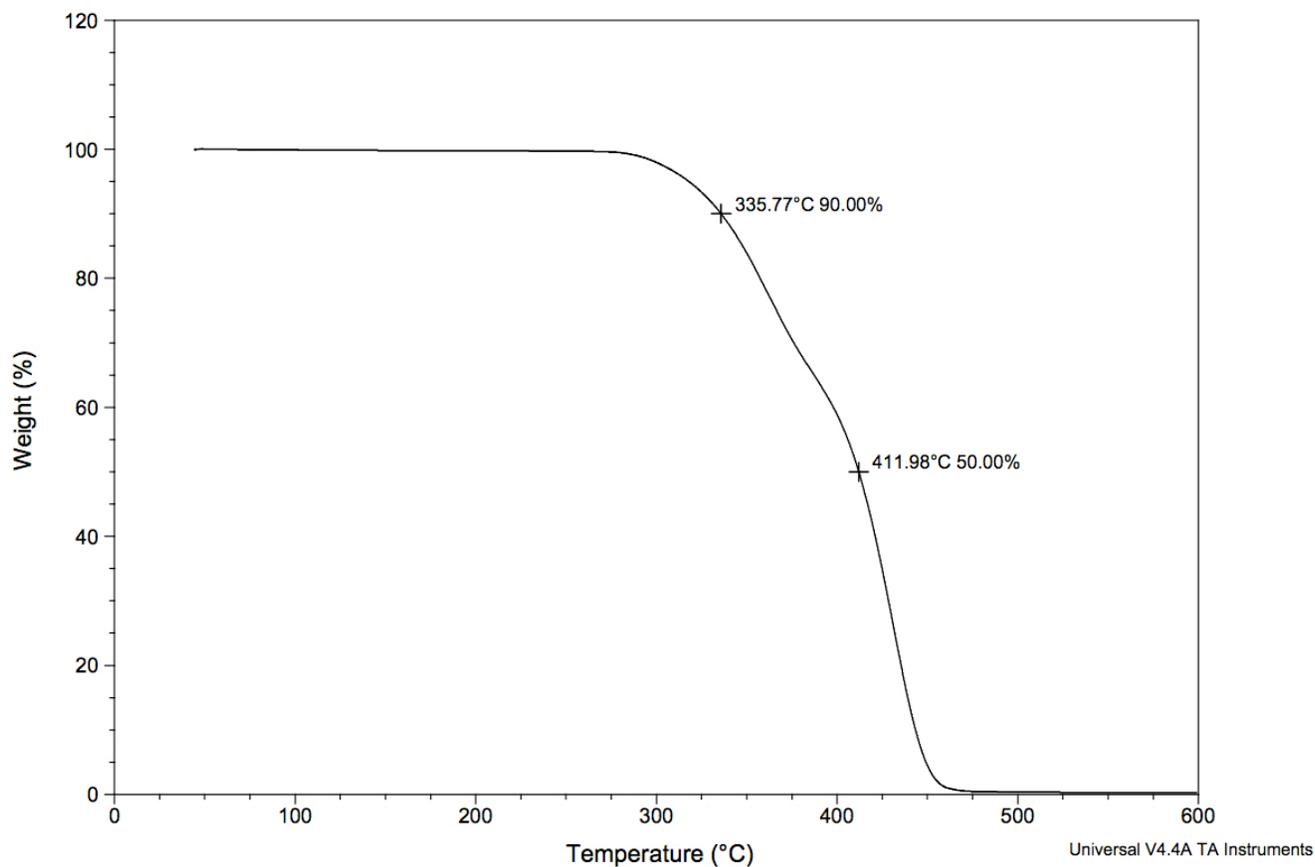


Figure S80. TGA Thermogram of polydecylene acetal, 10 gram scale-up (Table S1, entry 10).

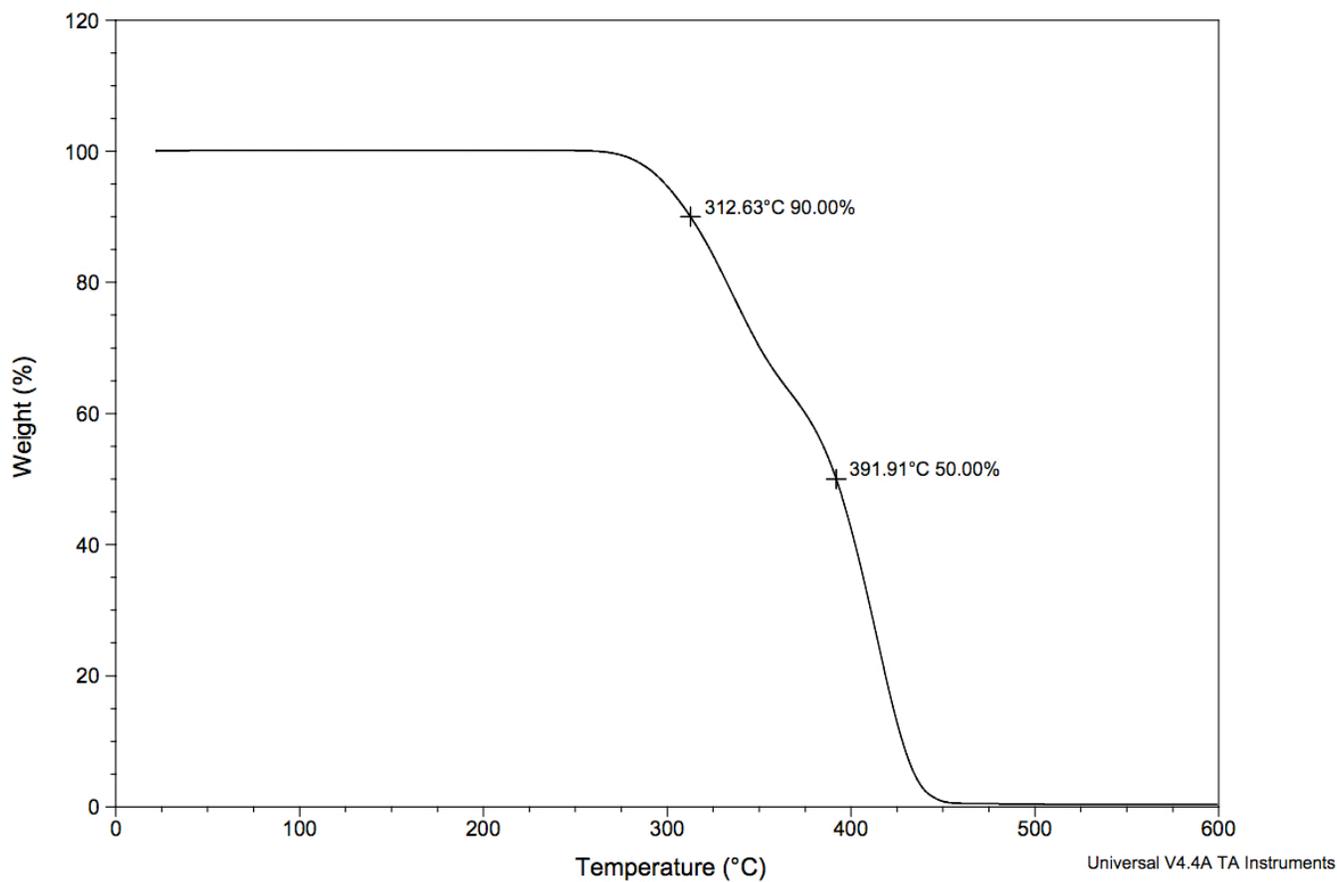


Figure S81. TGA Thermogram of polydecylene acetal, 50 gram scale-up (Table S1, entry 11).

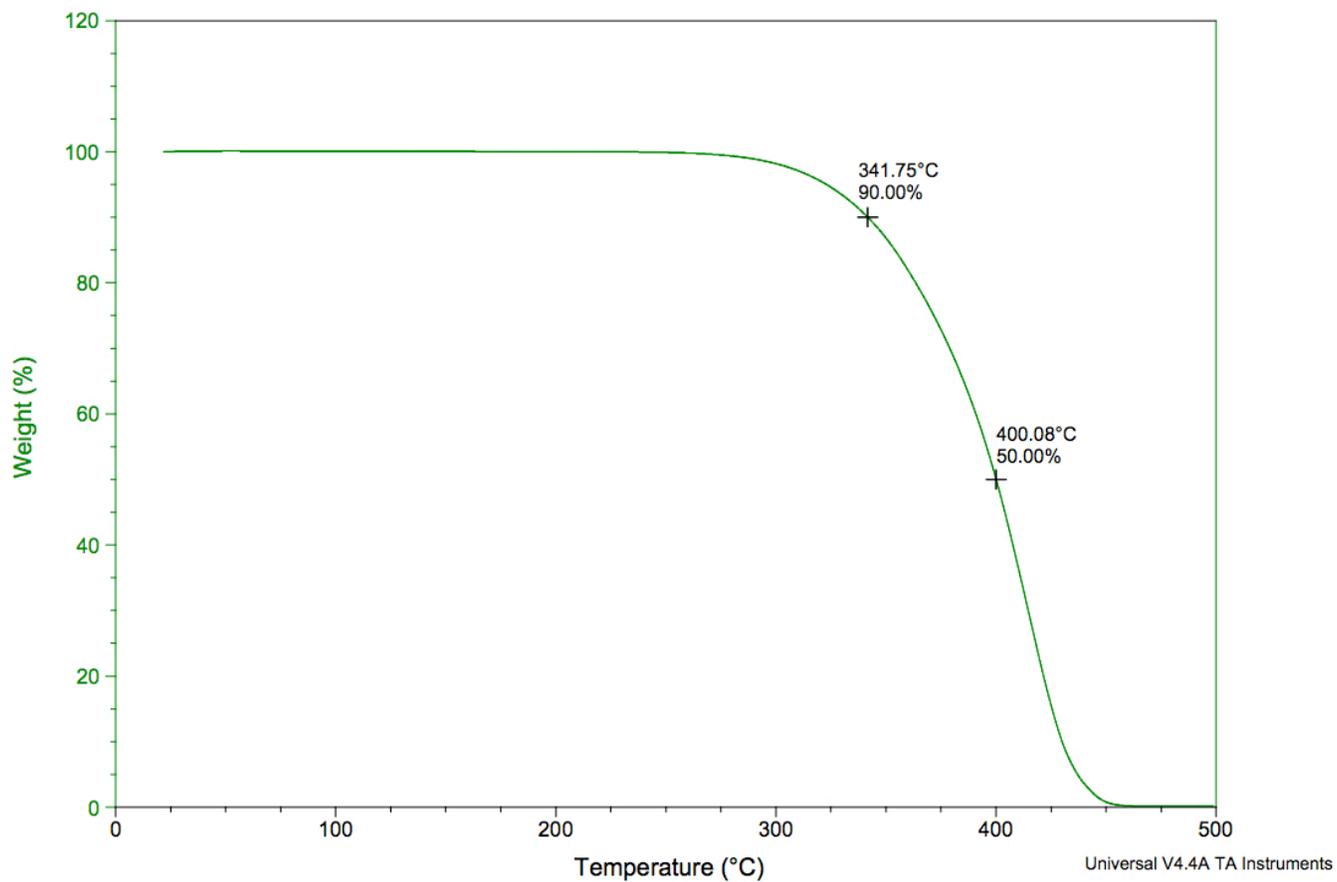


Figure S82. TGA Thermogram of polydecylene acetal, first iteration (Table S1, entry 12).

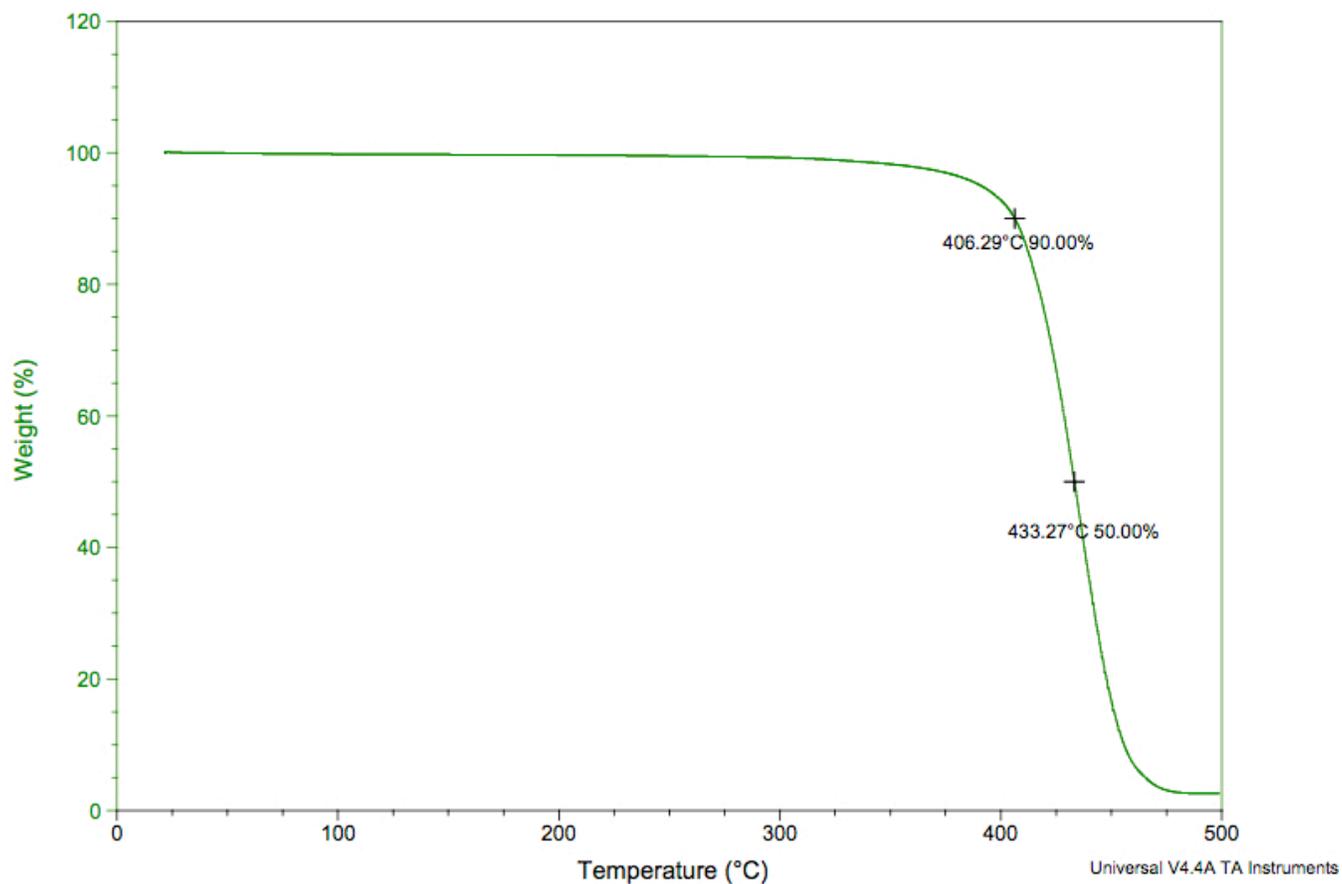


Figure S83. TGA Thermogram of polydecylene acetal, *second iteration* (Table S1, entry 13).

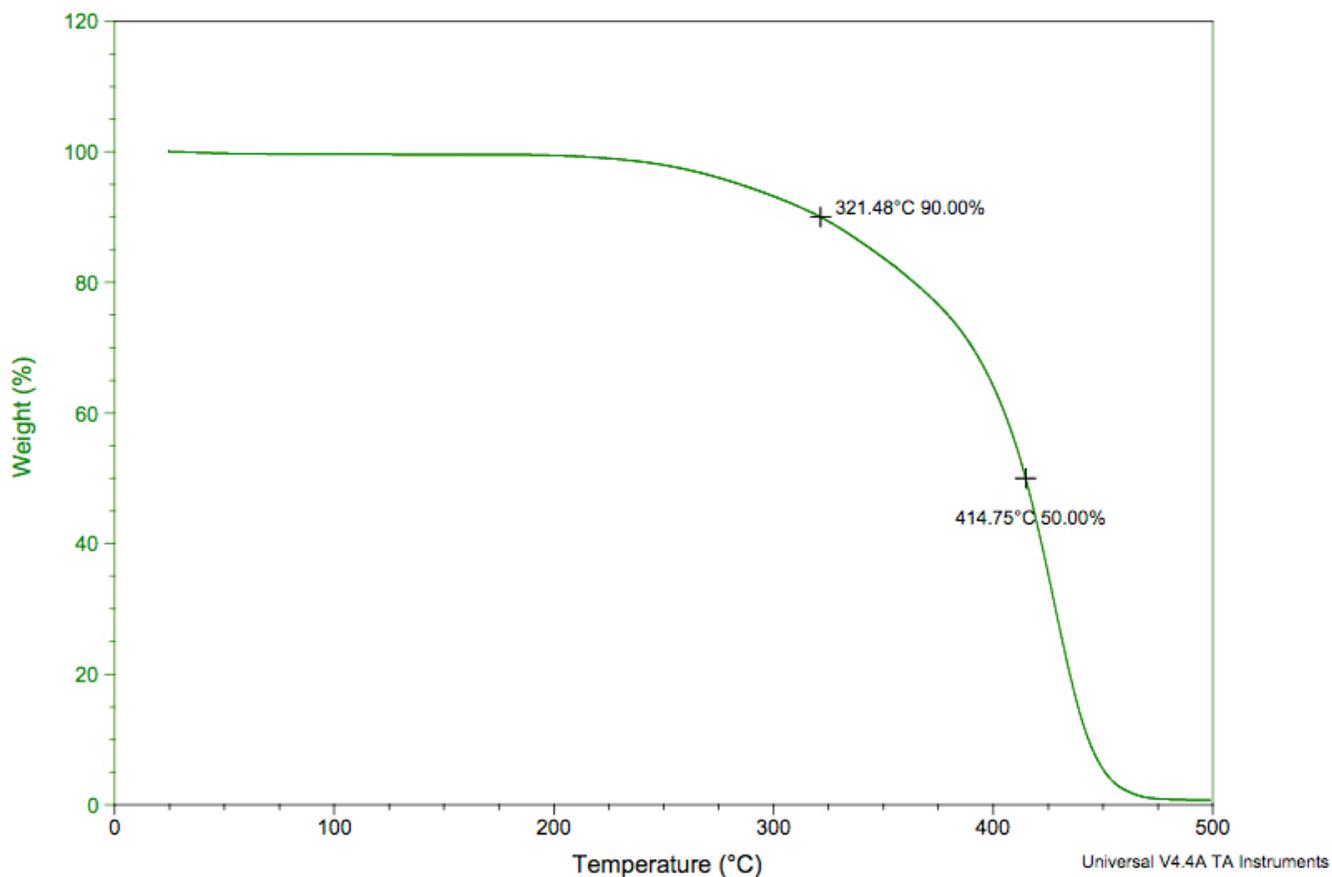


Figure S84. TGA Thermogram of polydodecylene acetal, *first iteration* (Table S1, entry 14).

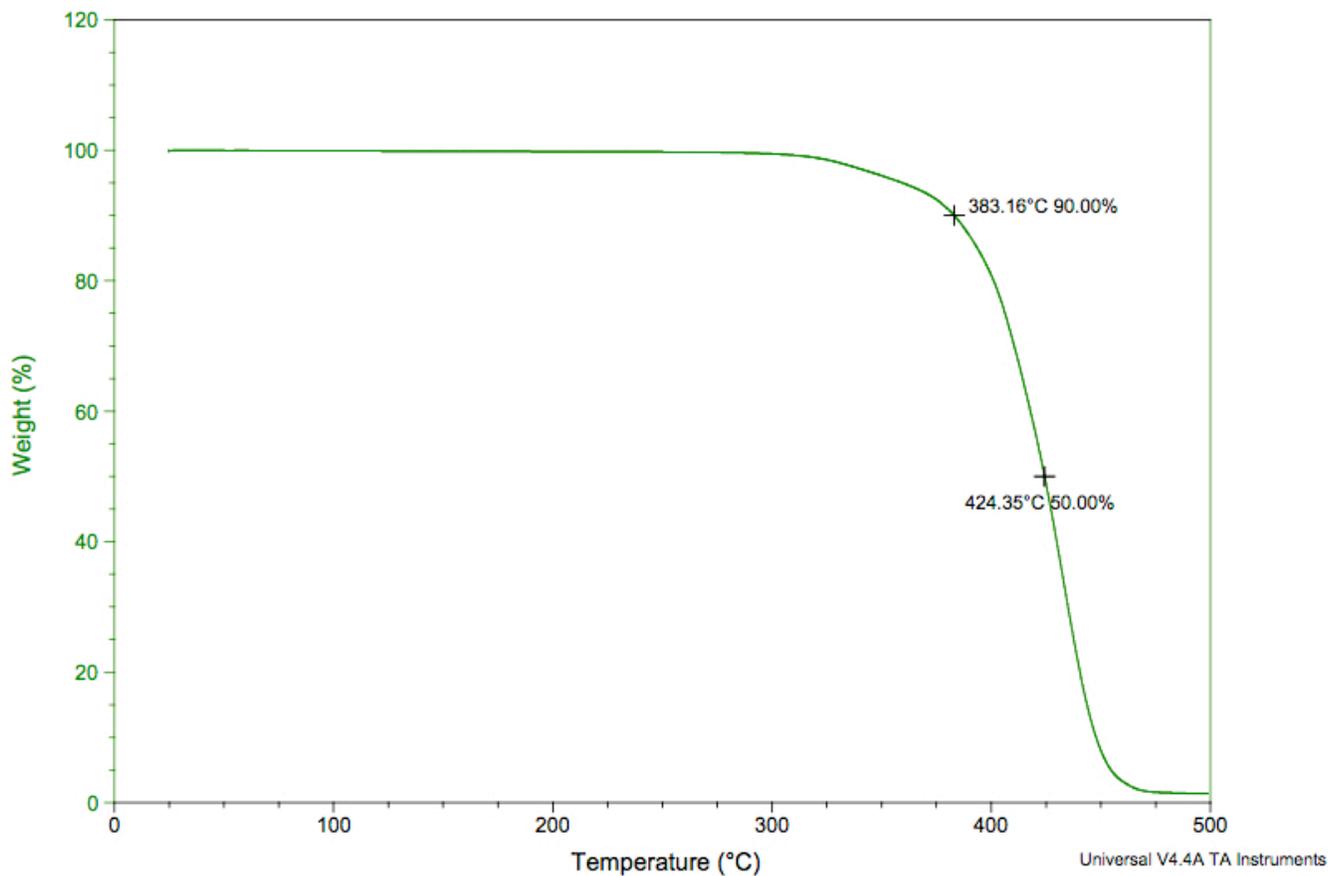


Figure S85. TGA Thermogram of polydodecylene acetal, *second iteration* (Table S1, entry 15).

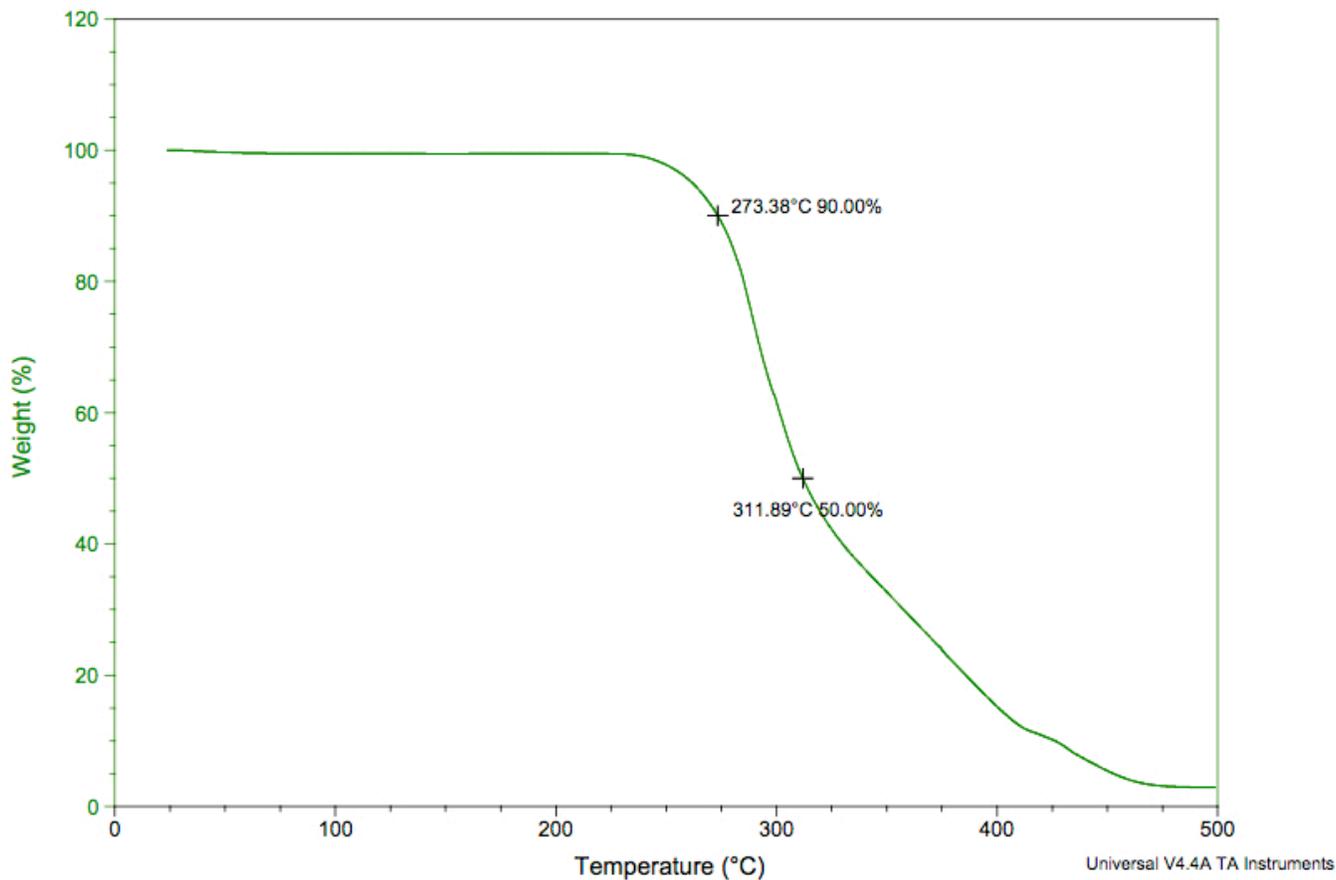


Figure S86. TGA Thermogram of polydecylene acetal, *from dimethoxymethane* (Table S1, entry 16).

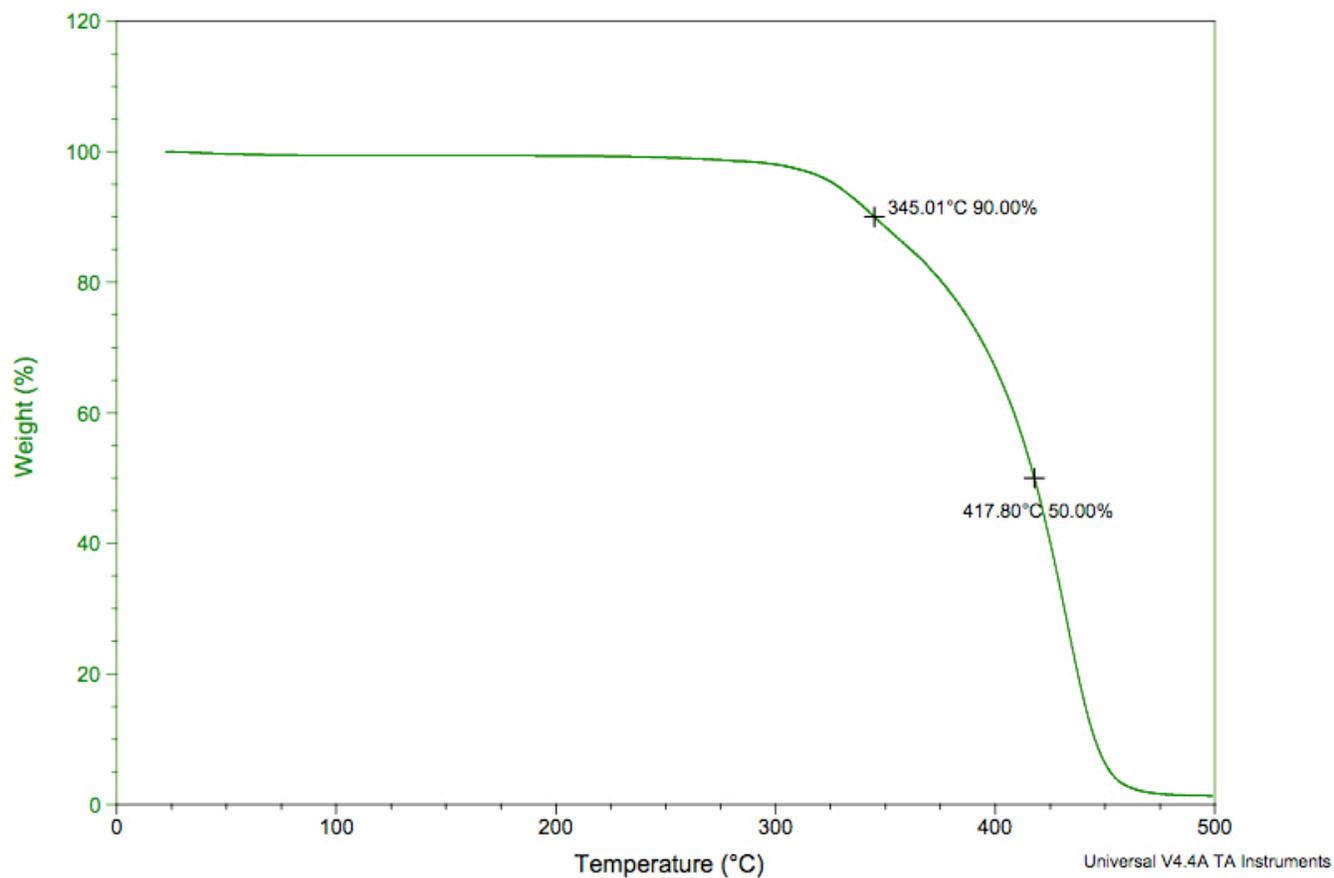


Figure S87. TGA Thermogram of polydodecylene acetal, *from dimethoxymethane* (Table S1, entry 17).

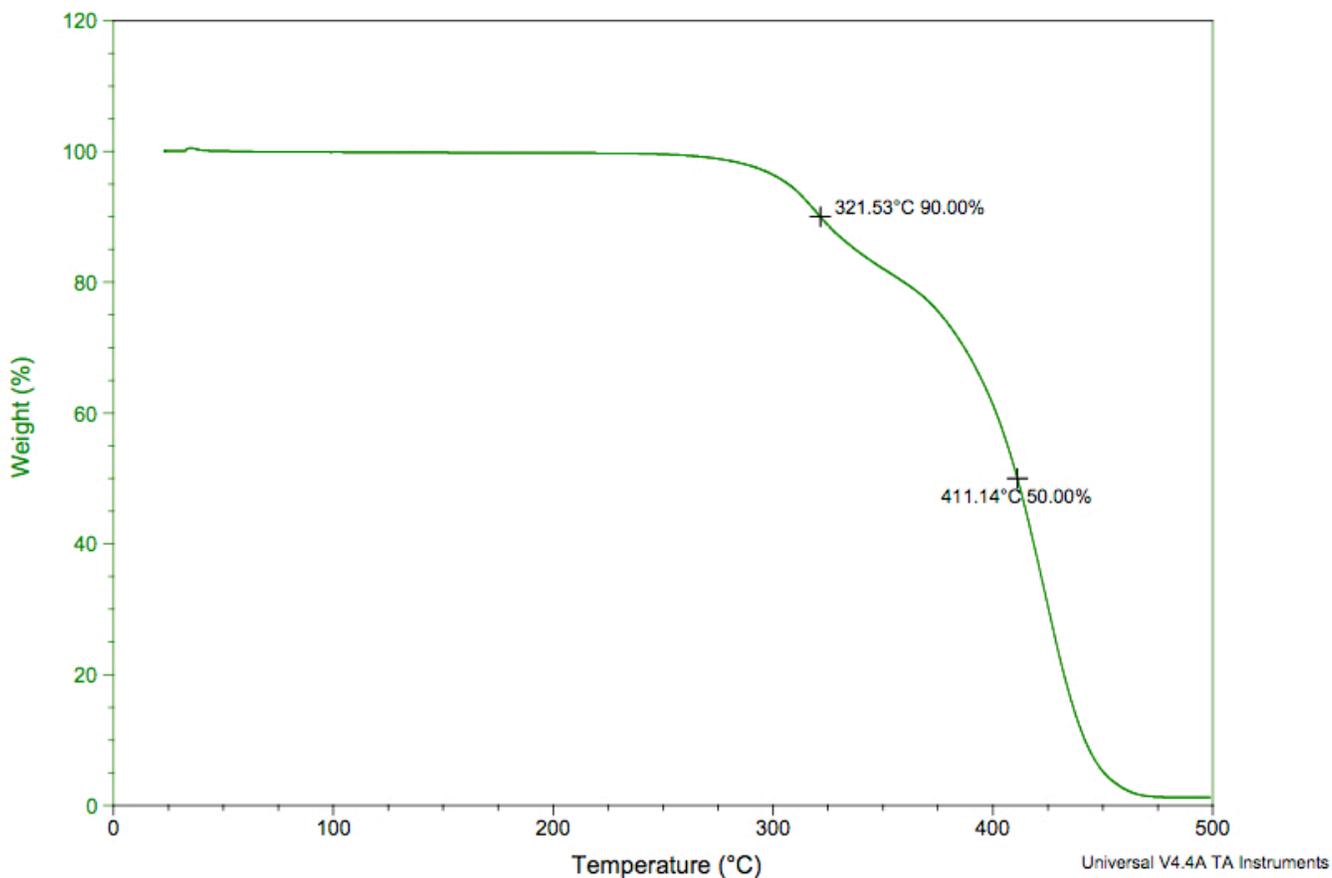


Figure S88. TGA Thermogram of polydecylene acetal, *from diethoxymethane:diol = 2:1* (Table S1, entry 18).

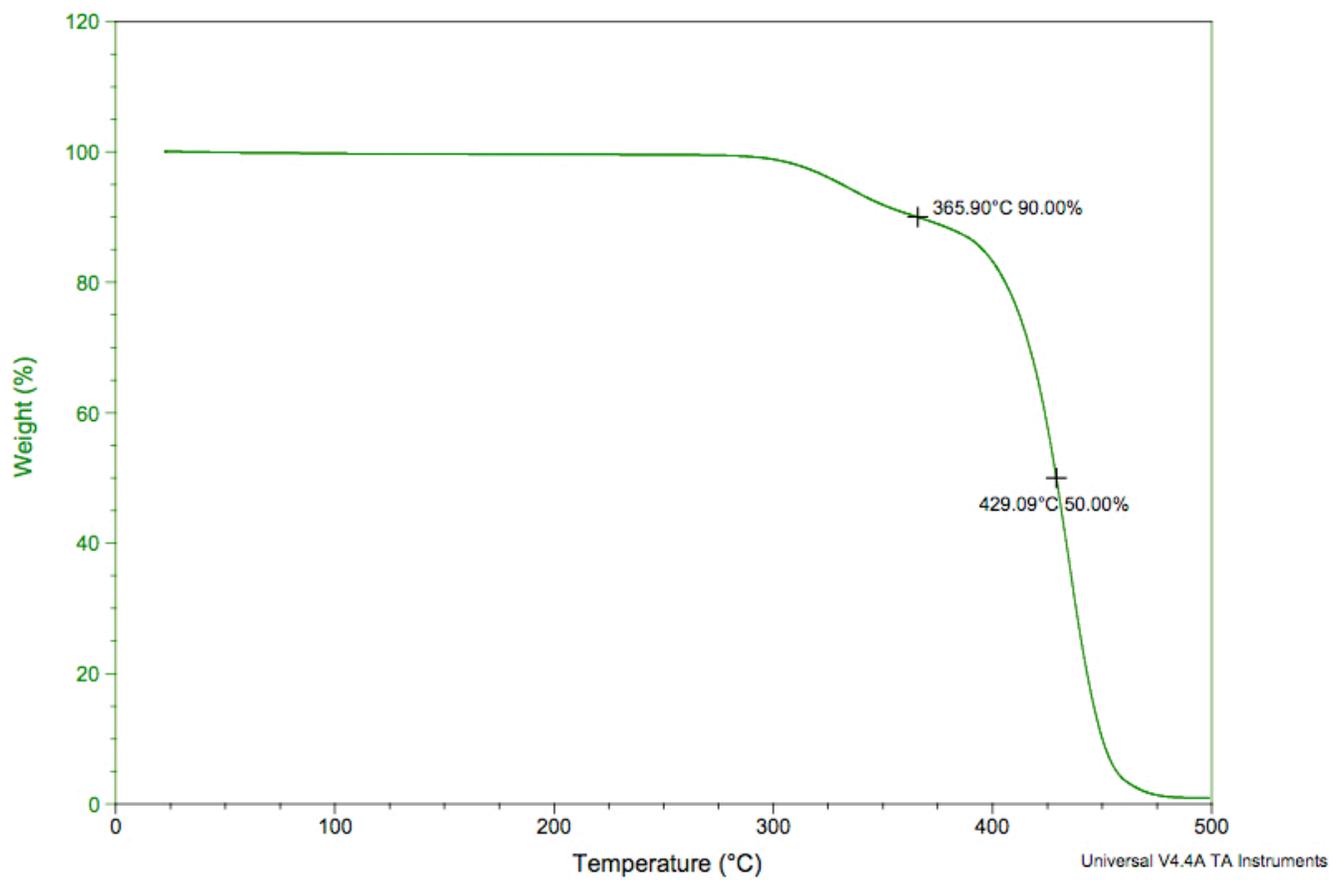


Figure S89. TGA Thermogram of polydecylene acetal, from dimethoxymethane:diol = 2:1 (Table S1, entry 19).

¹H NMR Spectra

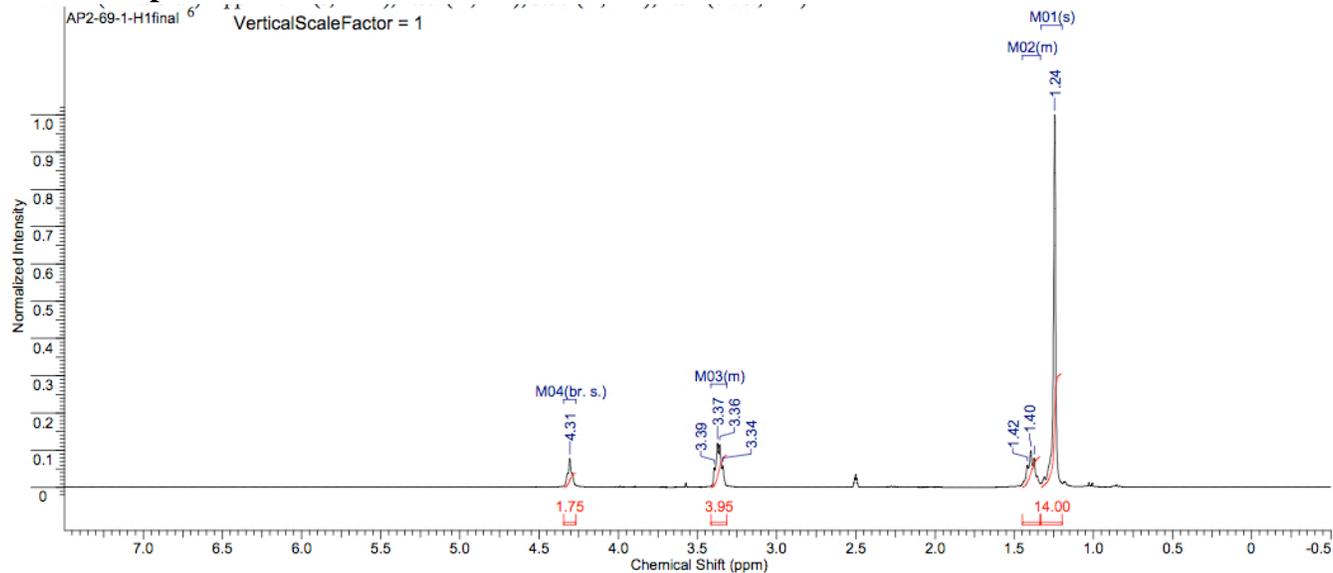


Figure S90. ¹H NMR spectrum of 1,11-undecanediol.

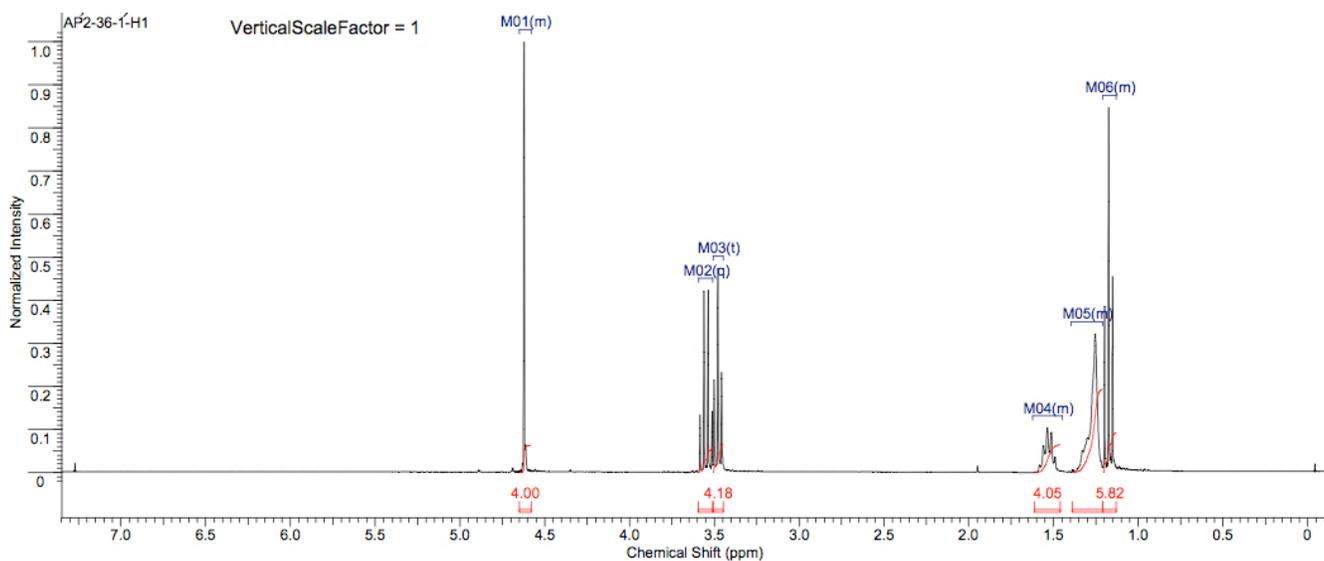


Figure S91. ¹H NMR spectrum of 3,5,16,18-tetraoxaicosane.

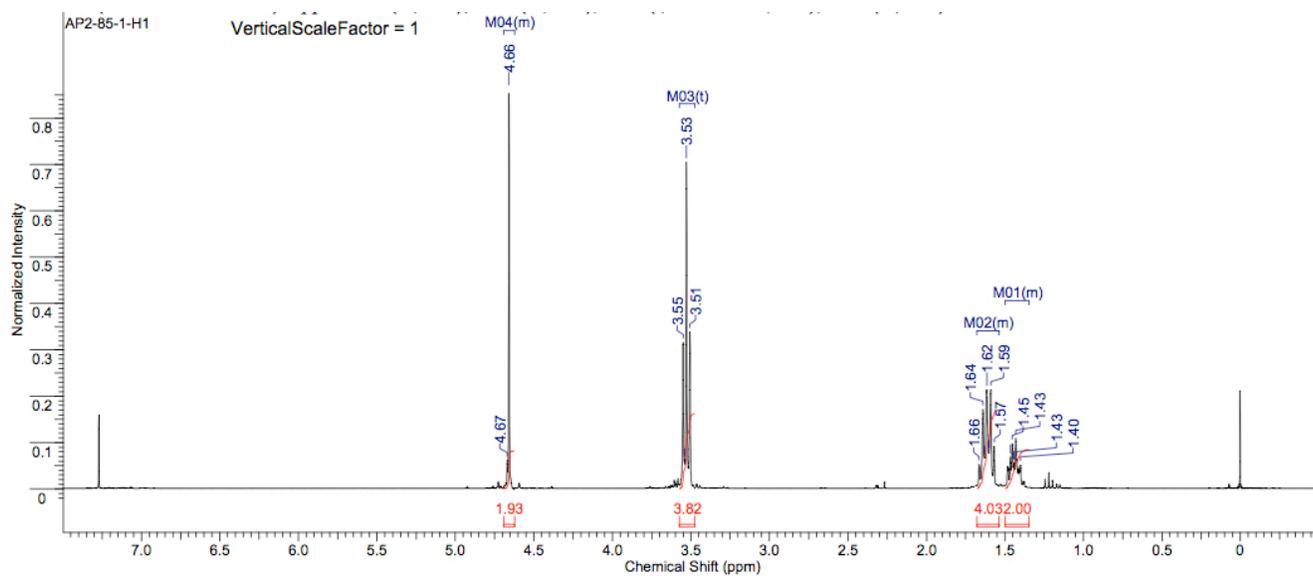


Figure S92. ¹H NMR spectrum of poly(pentylene acetal) (Table S1, entry 1).

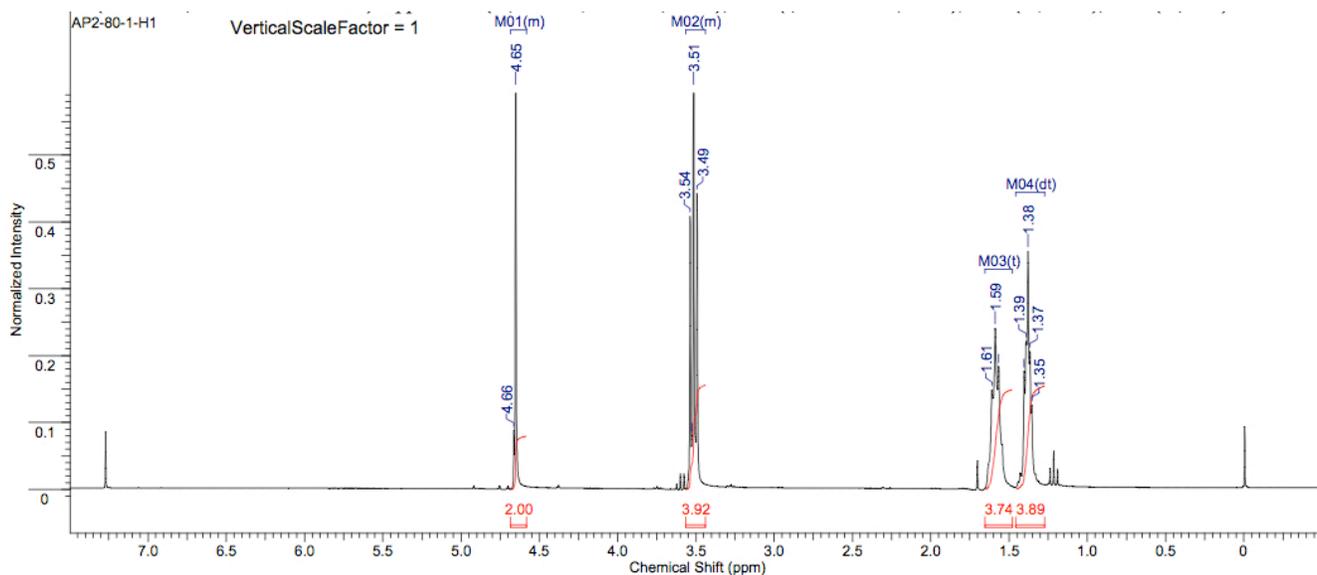


Figure S93. ¹H NMR spectrum of polyhexylene acetal (Table S1, entry 2).

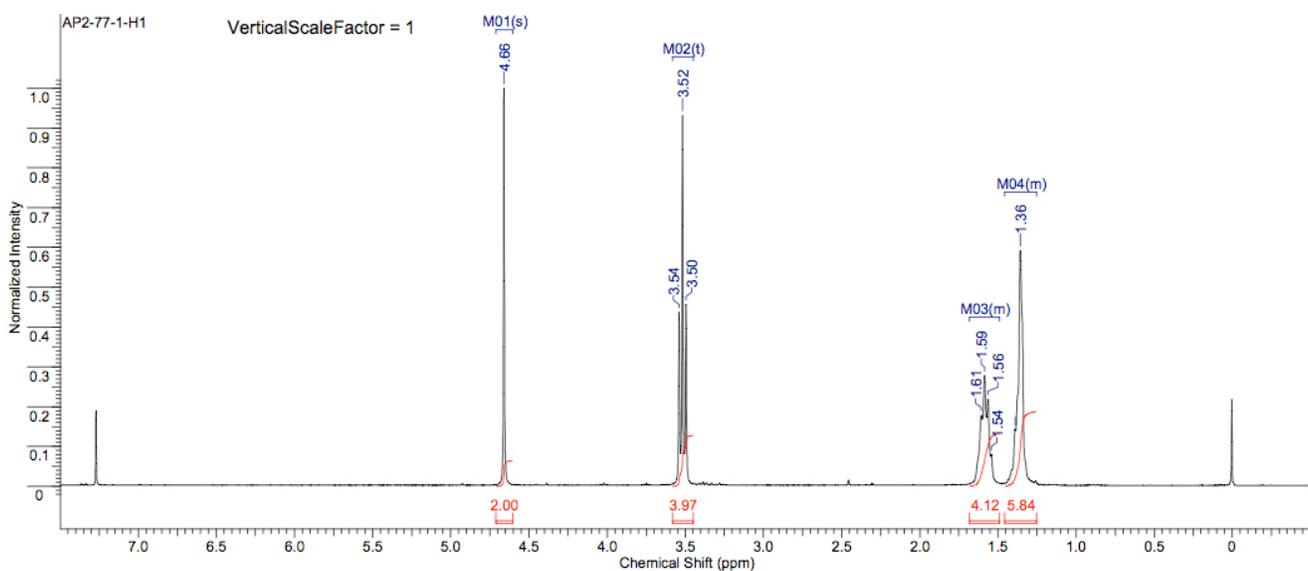


Figure S94. ¹H NMR spectrum of polyheptylene acetal (Table S1, entry 3).

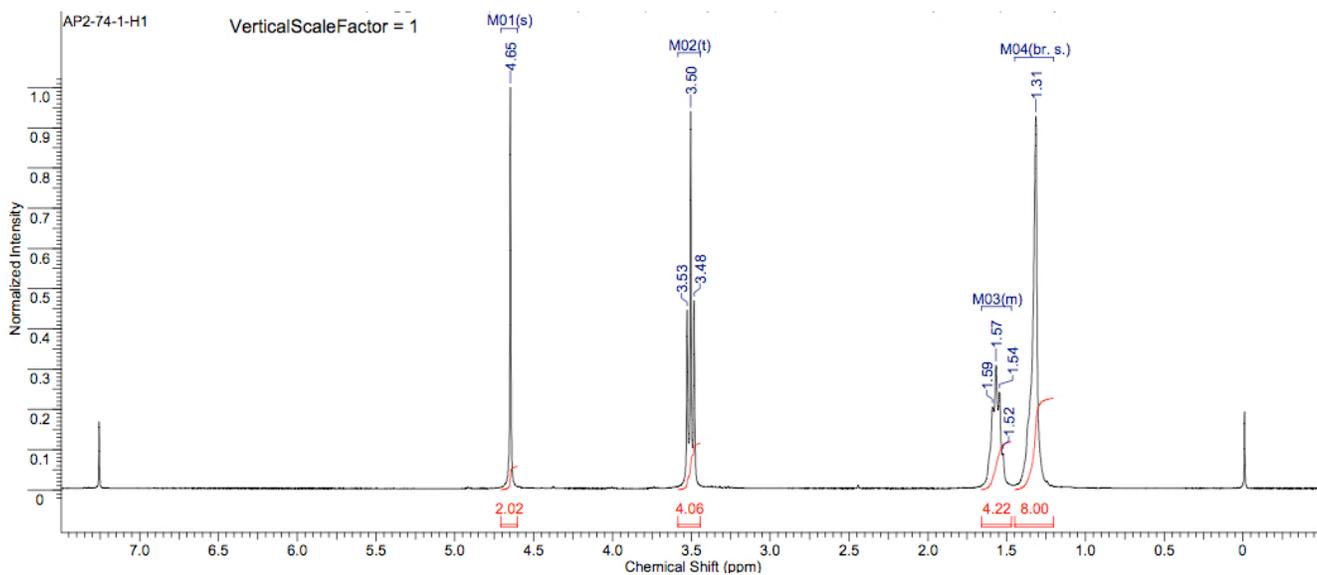


Figure S95. ¹H NMR spectrum of polyoctylene acetal (Table S1, entry 4).

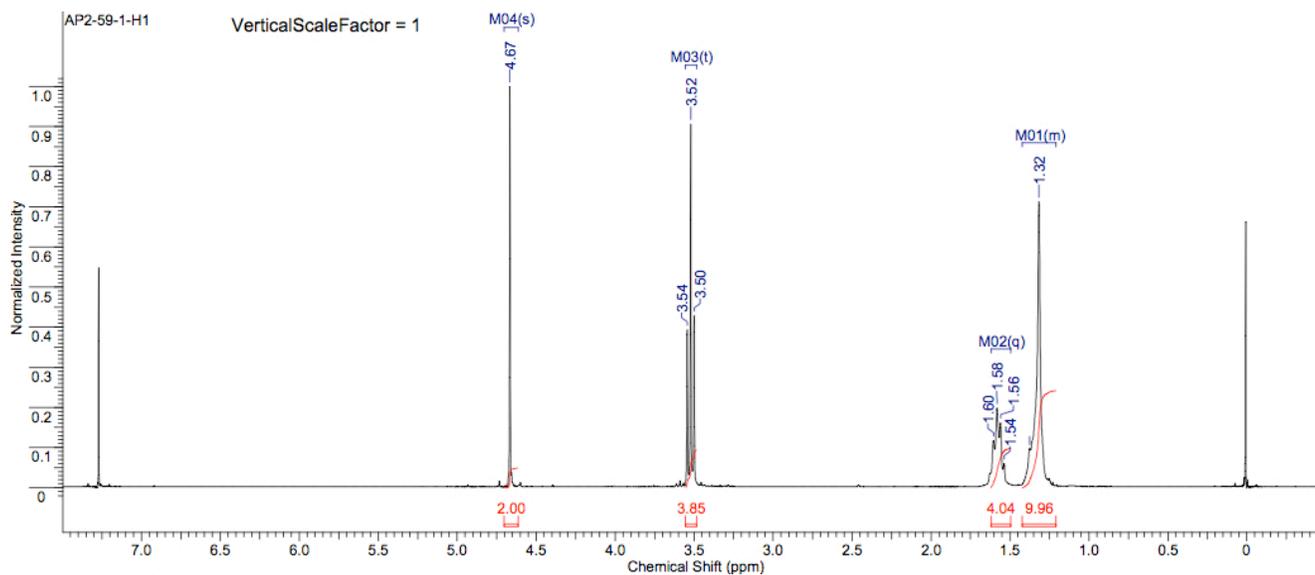


Figure S96. ¹H NMR spectrum of polynonylene acetal (Table S1, entry 5).

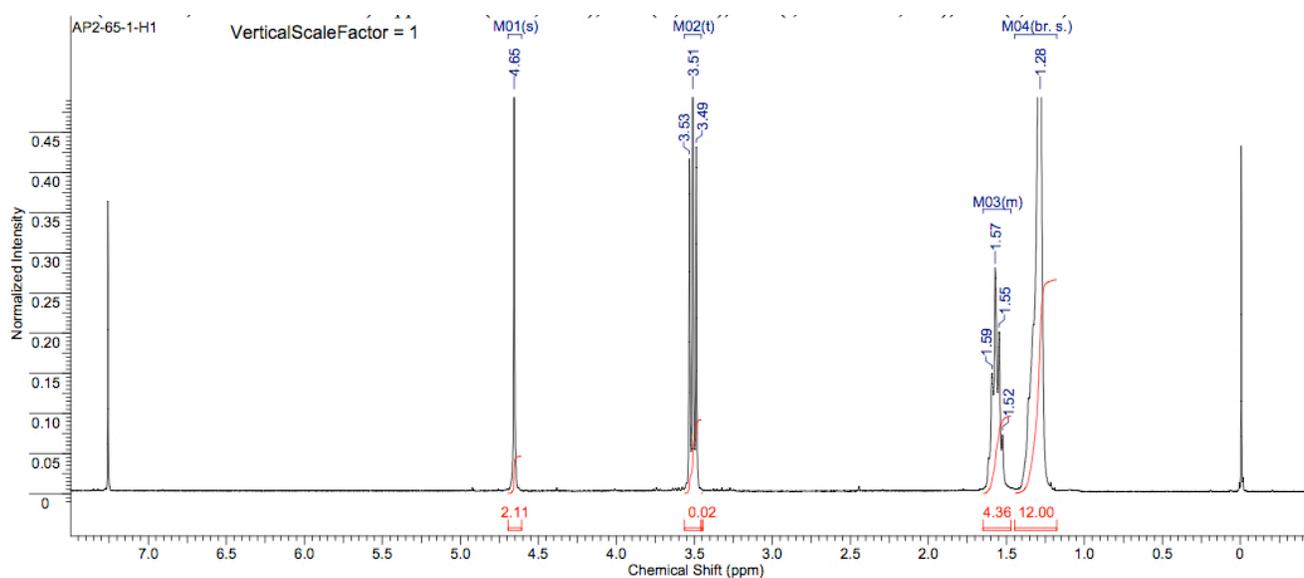


Figure S97. ¹H NMR spectrum of polydecylene acetal (Table S1, entry 6).

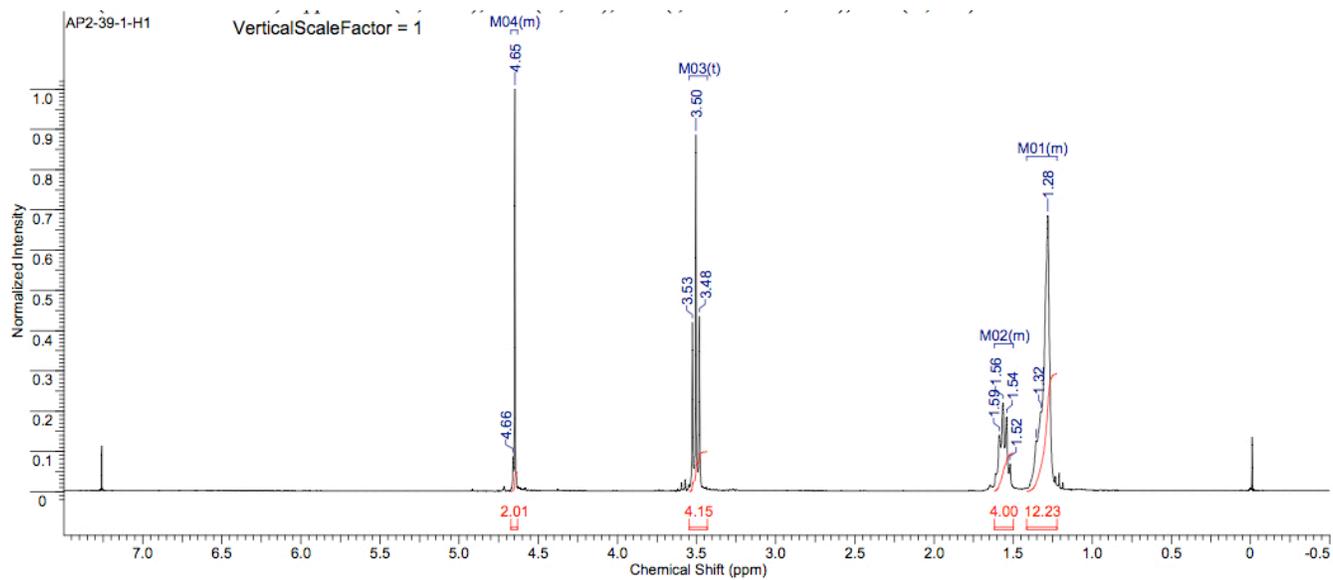


Figure S98. ¹H NMR spectrum of polydecylene acetal, from the two-pot synthesis (Table S1, entry 7).

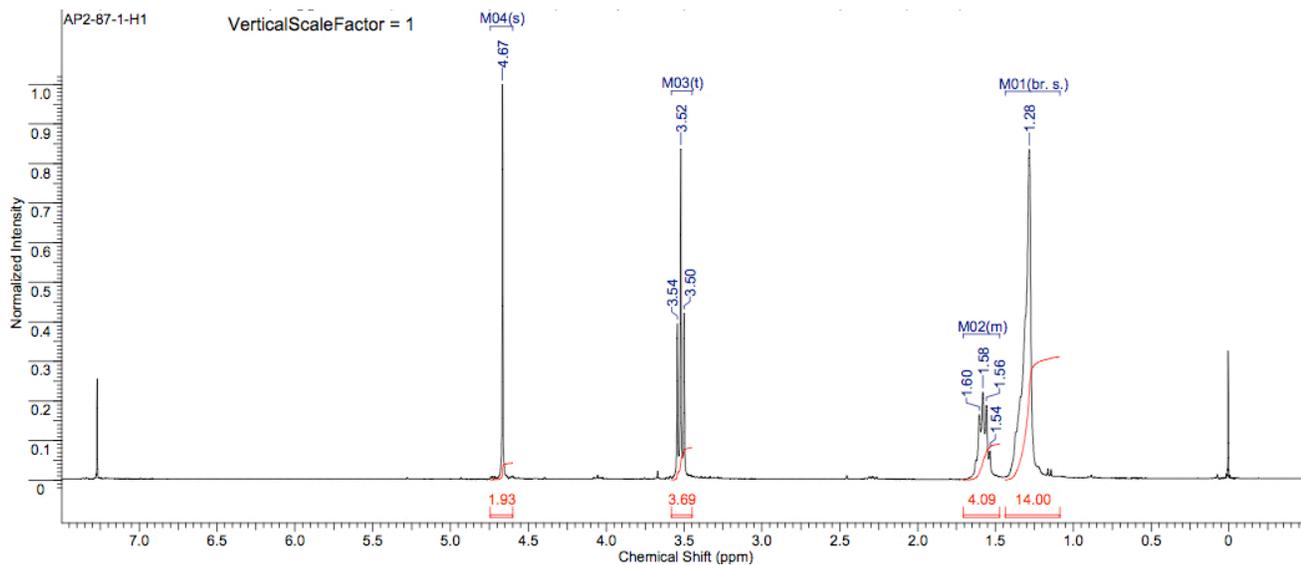


Figure S99. ^1H NMR spectrum of polyundecylene acetal (Table S1, entry 8).

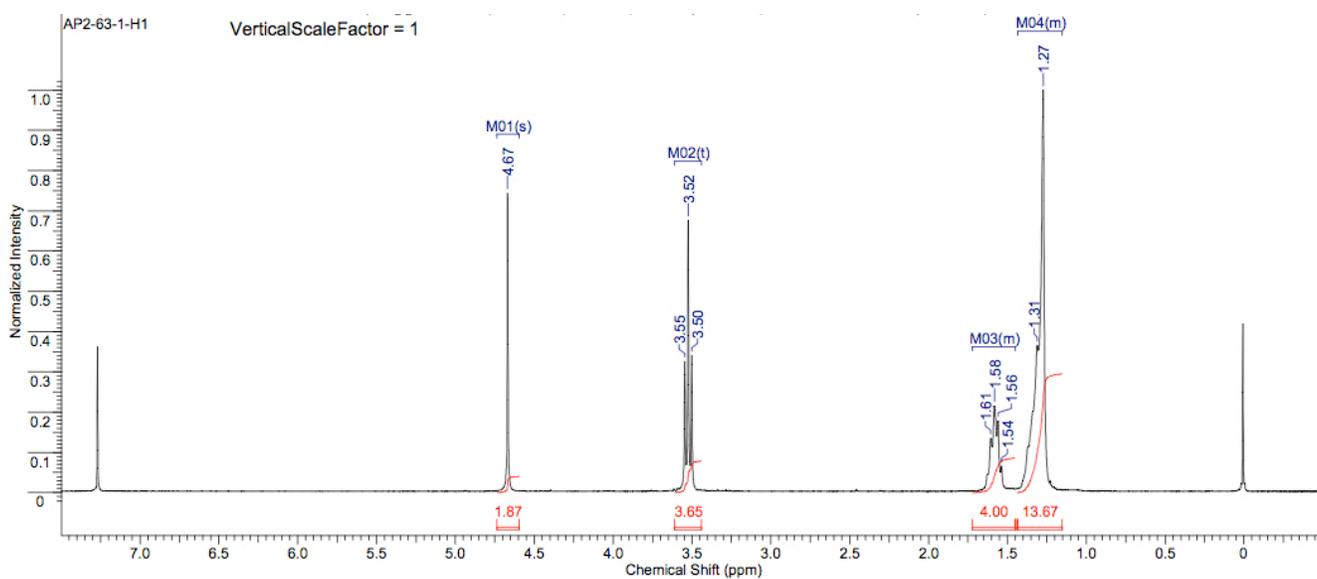


Figure S100. ^1H NMR spectrum of polydodecylene acetal (Table S1, entry 9).

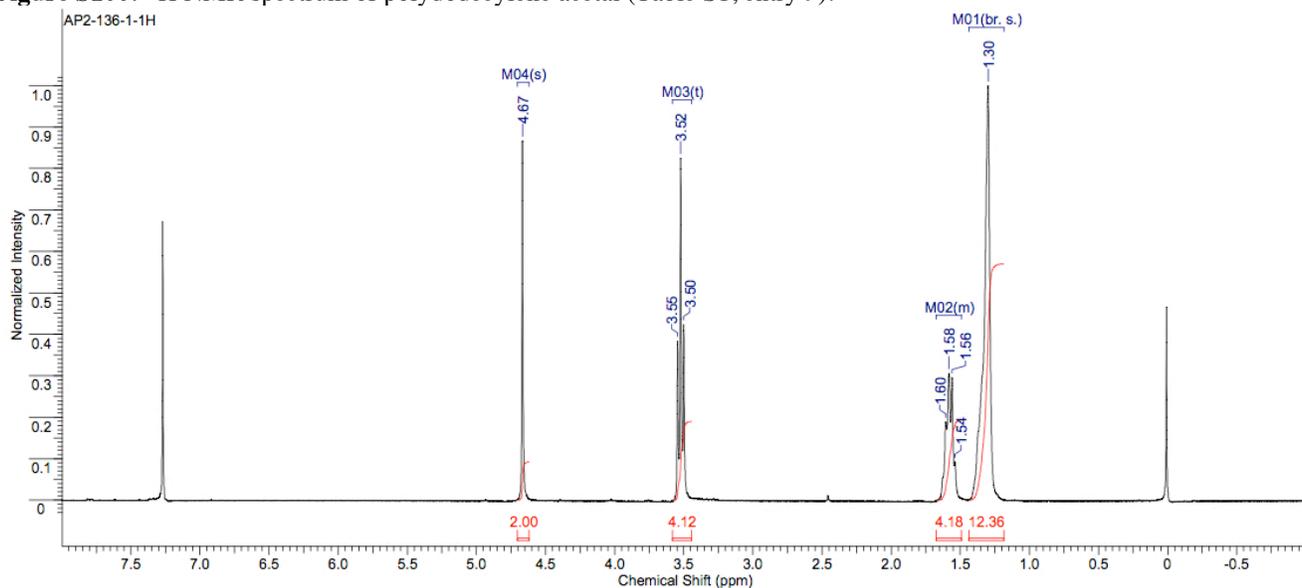


Figure S101. ^1H NMR spectrum of polydecylene acetal, 10 gram scale-up (Table S1, entry 10).

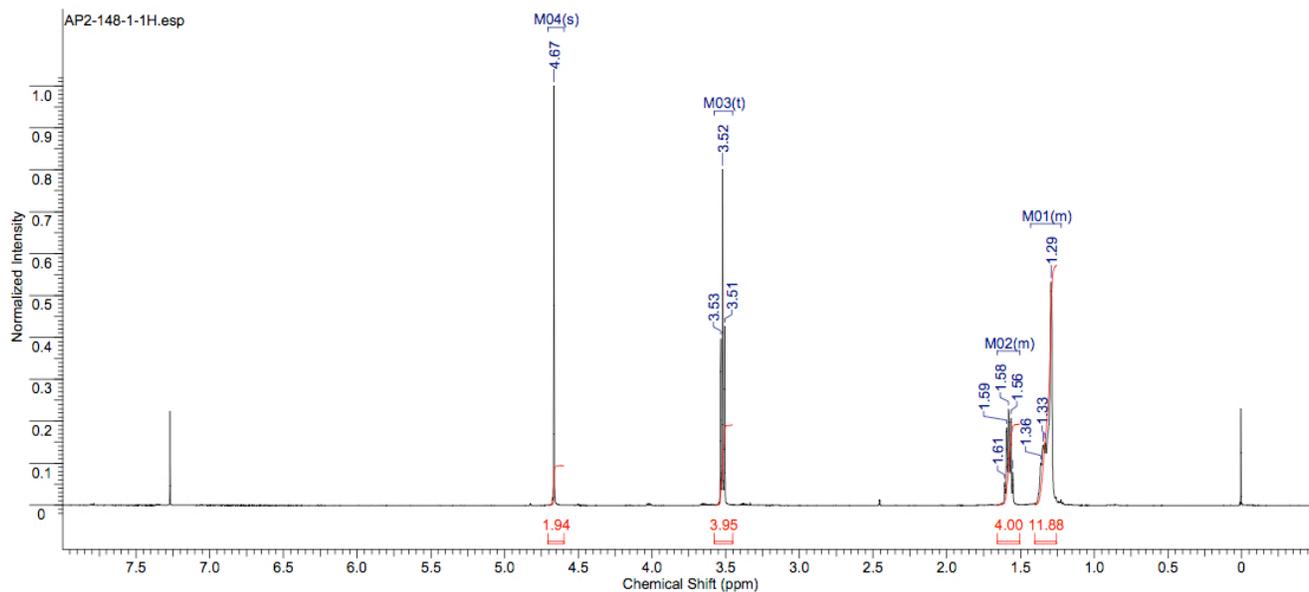


Figure S102. ¹H NMR spectrum of polydecylene acetal, 50 gram scale-up (Table S1, entry 11).

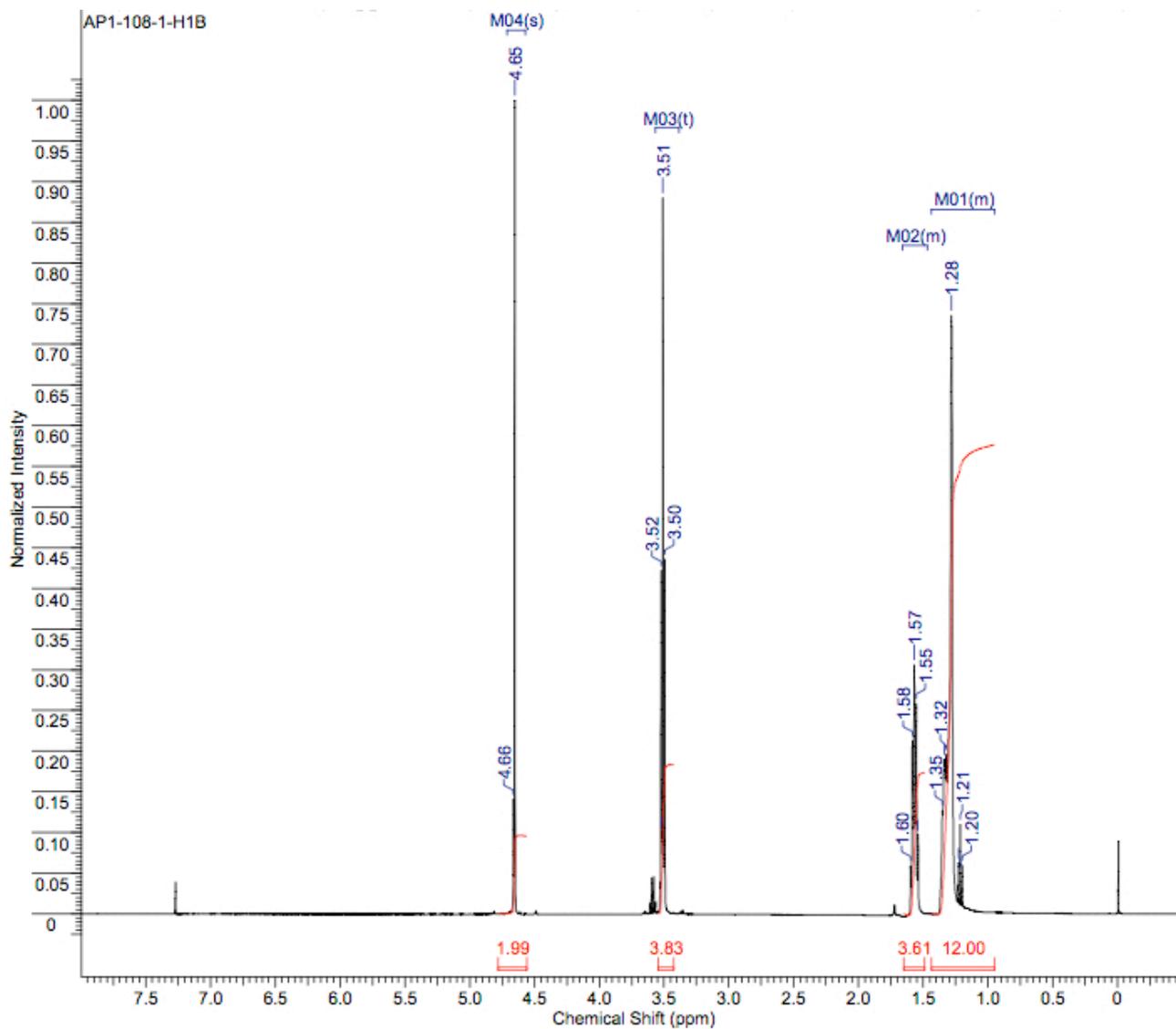


Figure S103. ¹H NMR spectrum of polydecylene acetal, first iteration (Table S1, entry 12).

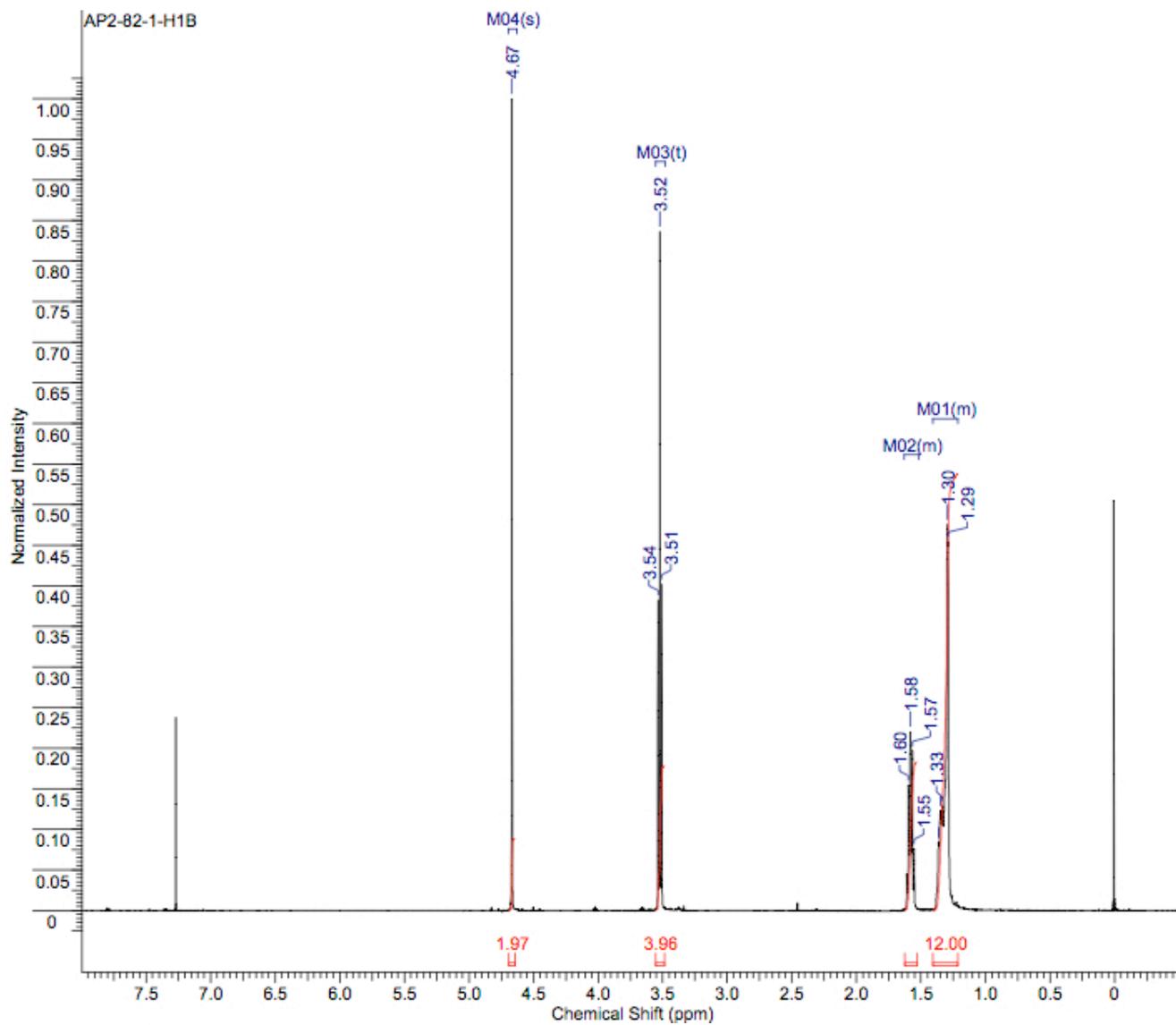


Figure S104. ¹H NMR spectrum of polydecylene acetal, *second iteration* (Table S1, entry 13).

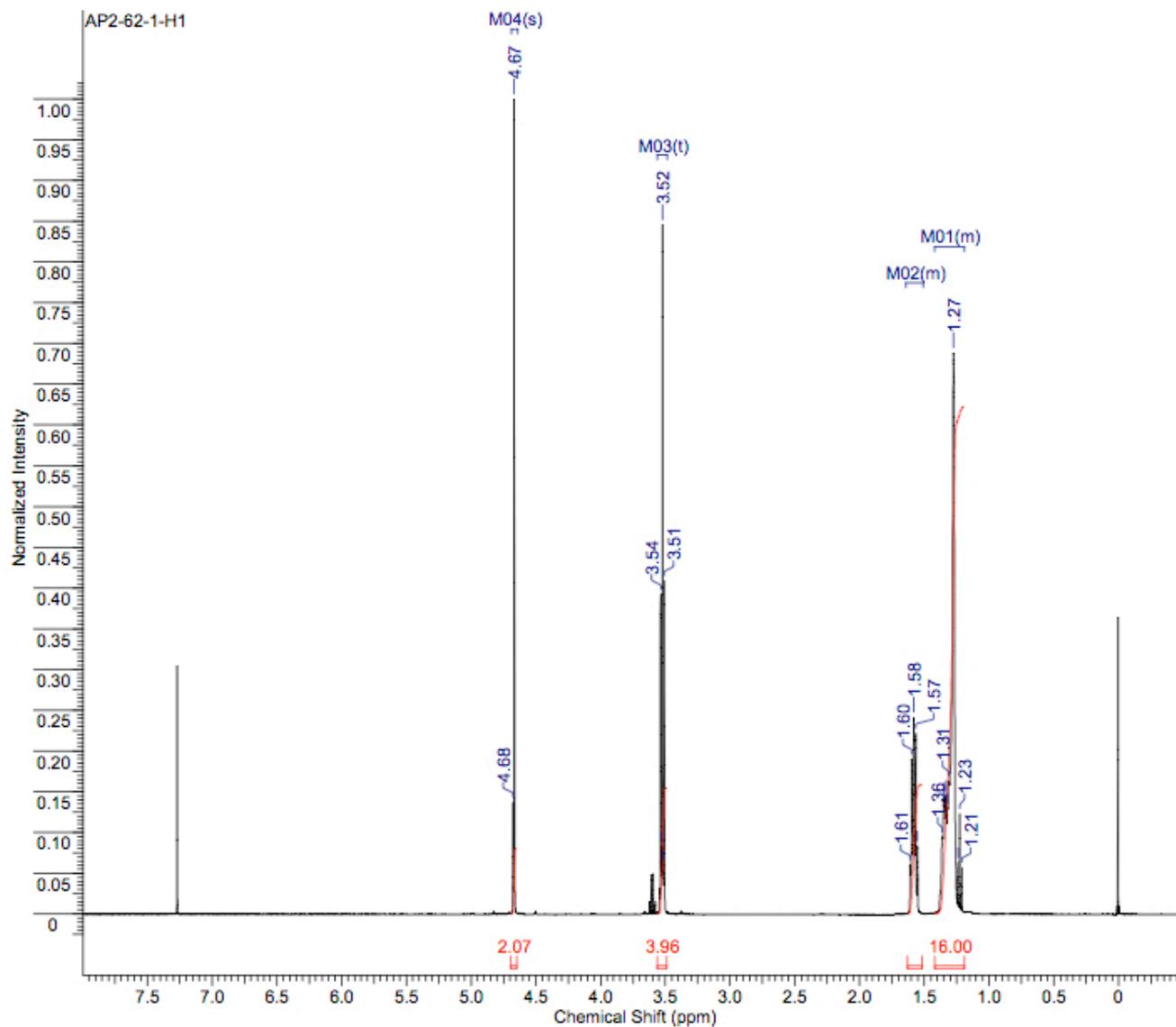


Figure S105. ^1H NMR spectrum of polydodecylene acetal, *first iteration* (Table S1, entry 14).

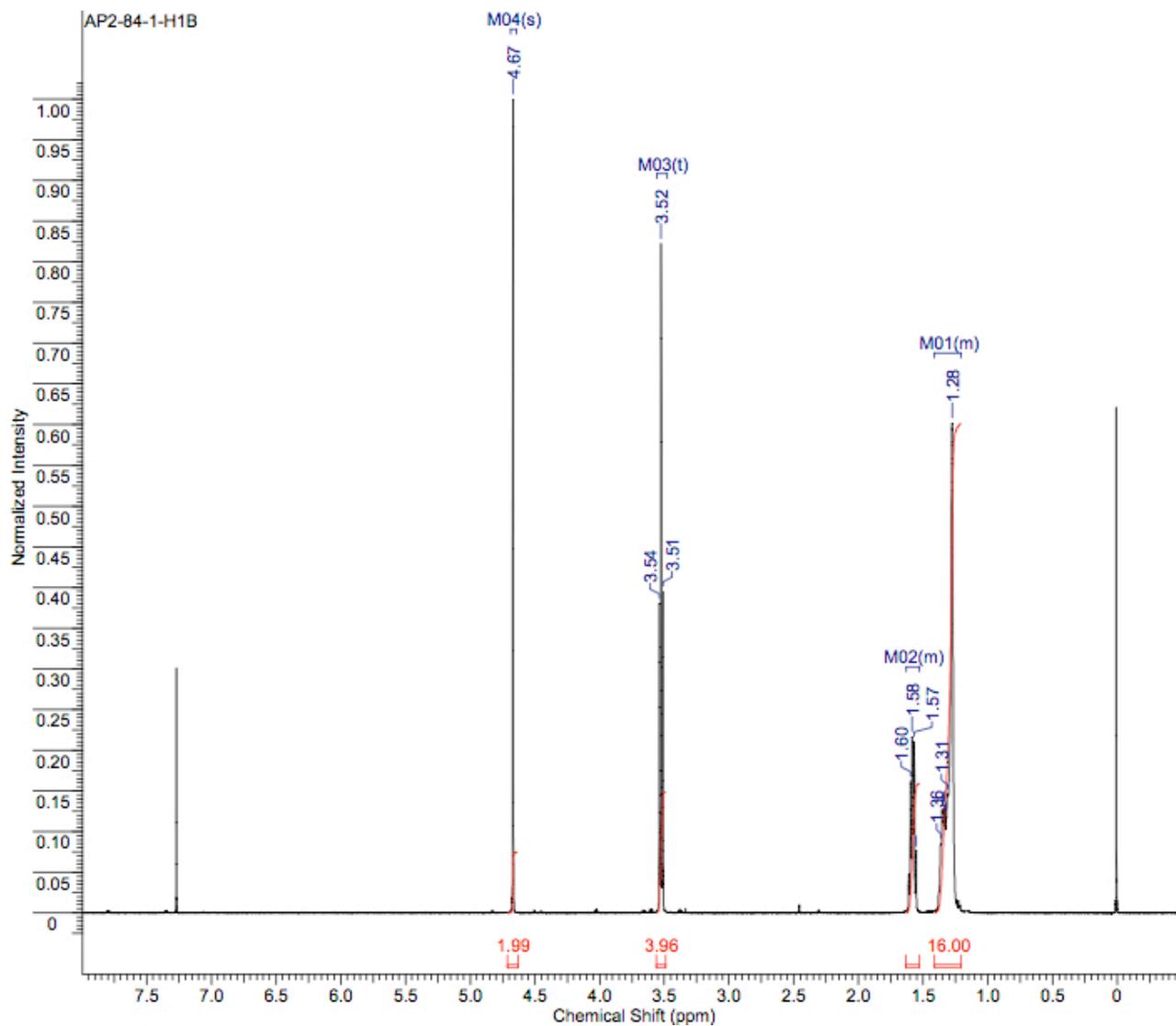


Figure S106. ¹H NMR spectrum of polydodecylene acetal, *second iteration* (Table S1, entry 15).

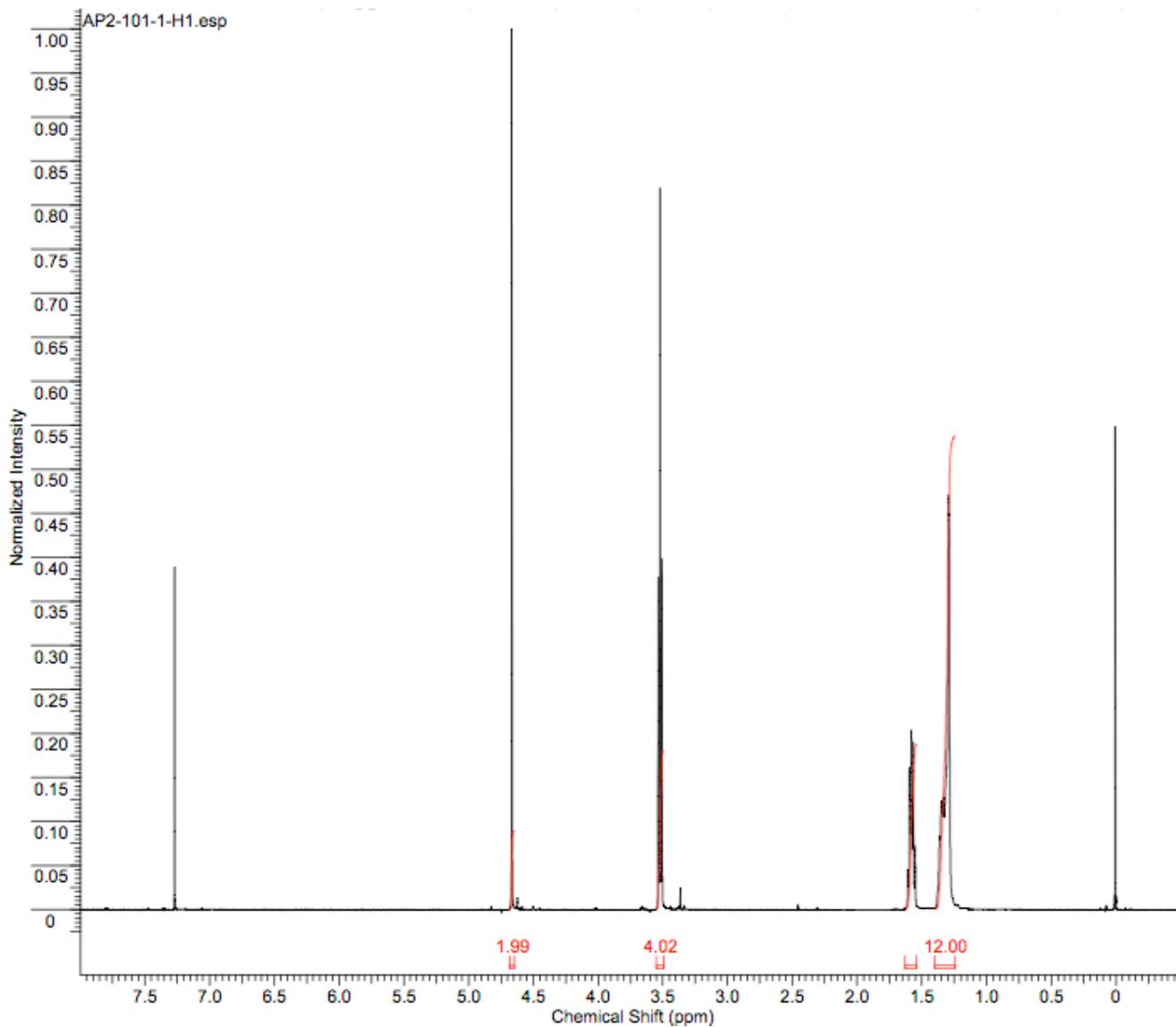


Figure S107. ¹H NMR spectrum of polydecylene acetal, *from dimethoxymethane* (Table S1, entry 16).

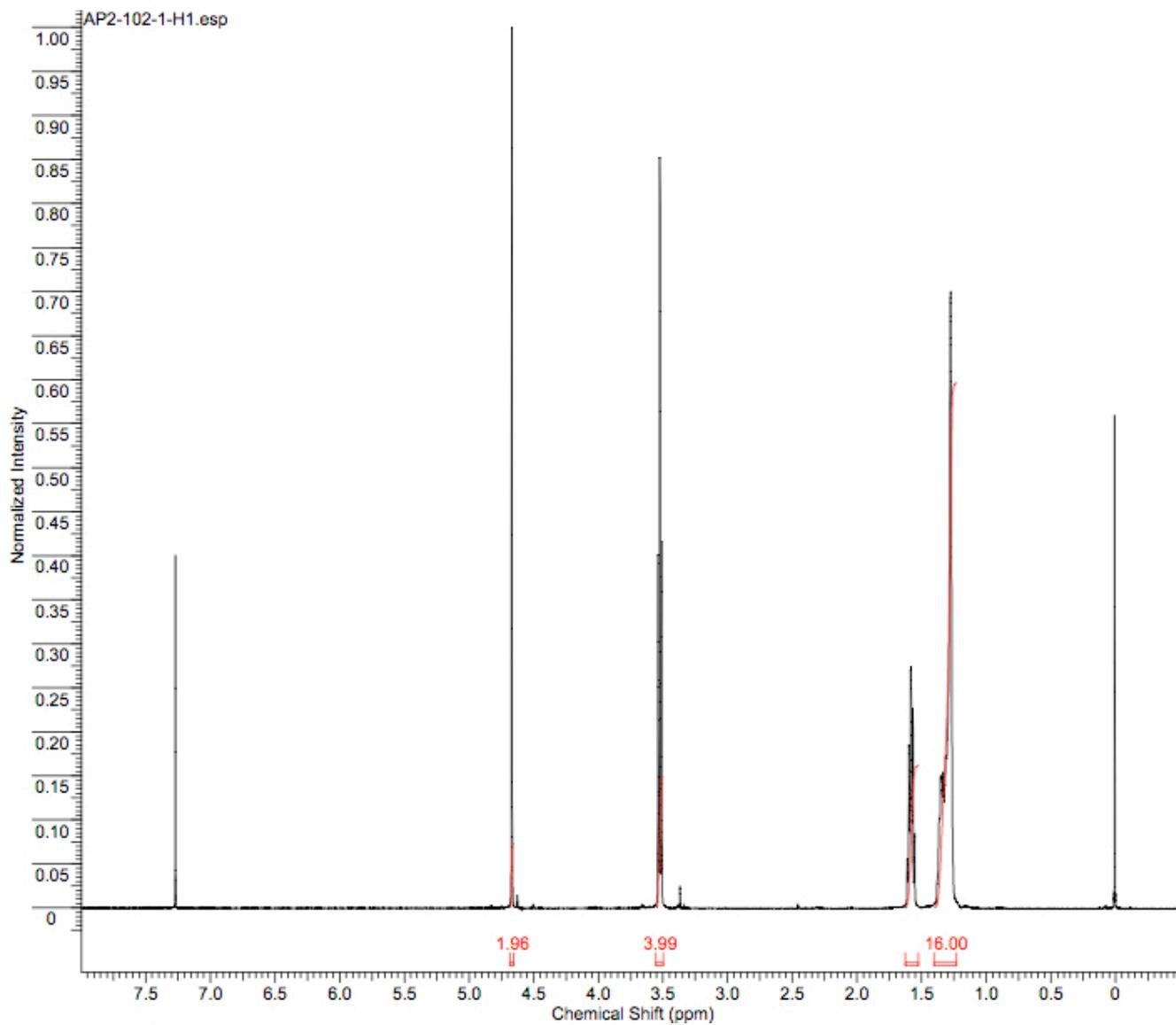


Figure S108. ¹H NMR spectrum of polydodecylene acetal, from dimethoxymethane (Table S1, entry 17).

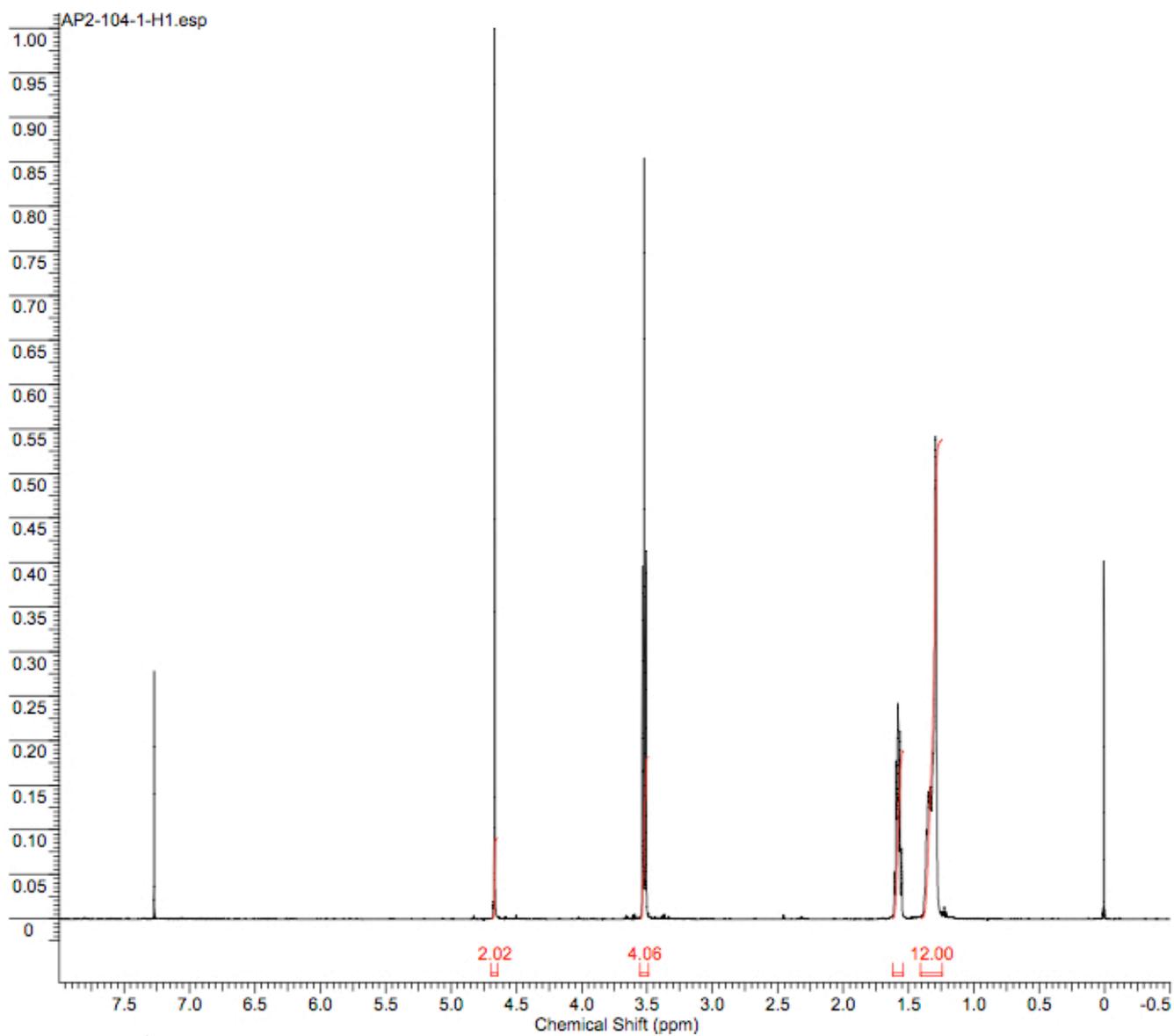


Figure S109. ¹H NMR spectrum of polydecylene acetal, from diethoxymethane:diol = 2:1 (Table S1, entry 18).

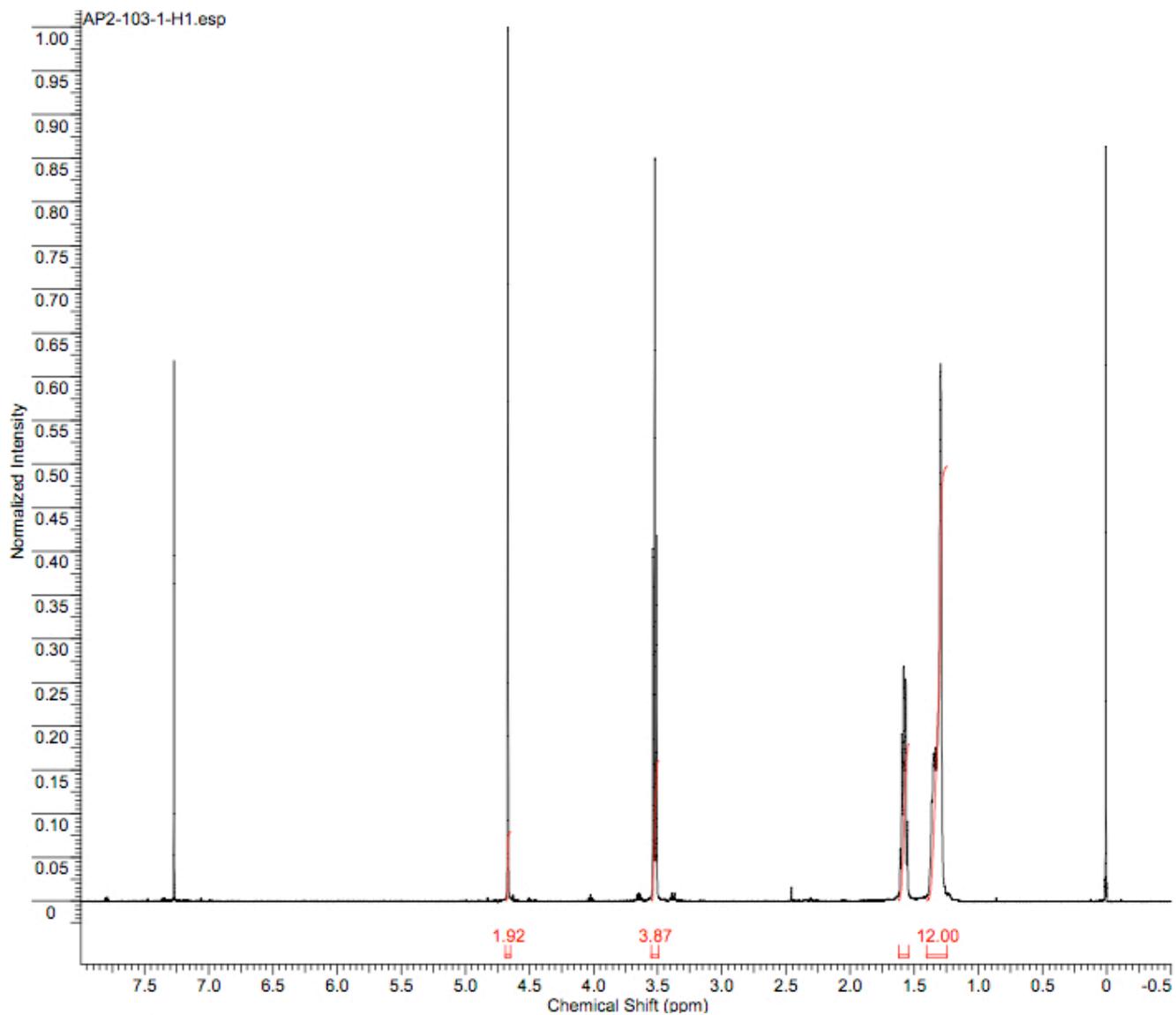


Figure S110. ^1H NMR spectrum of polydecylene acetal, from dimethoxymethane:diol = 2:1 (Table S1, entry 19).

¹³C NMR Spectra

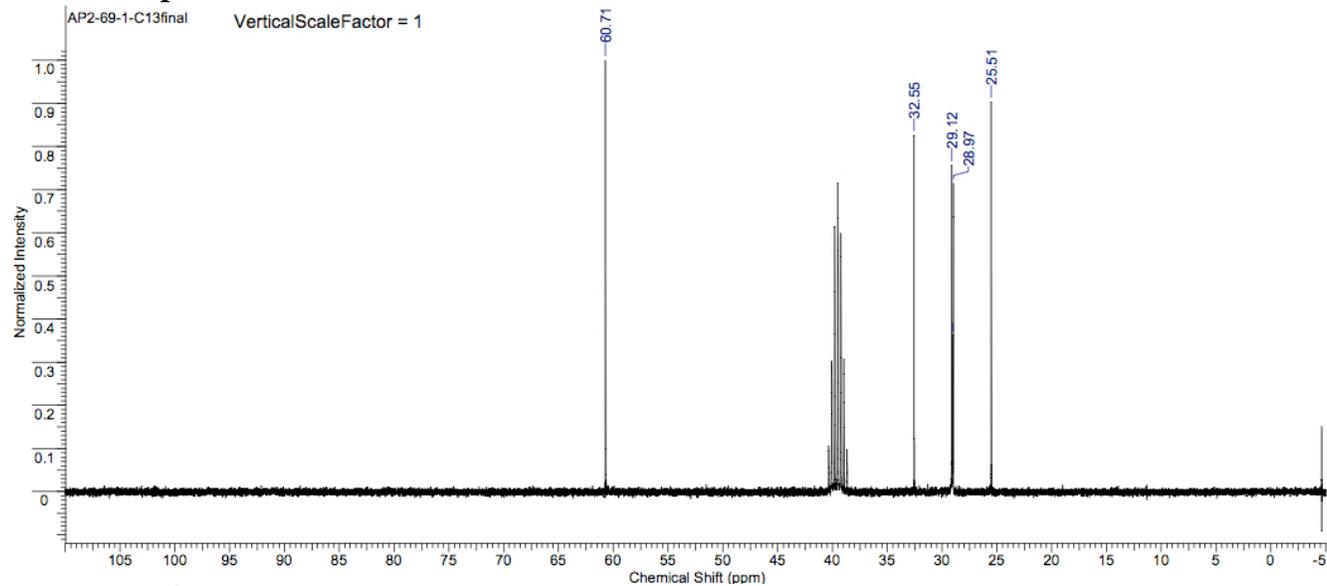


Figure S111. ¹³C NMR spectrum of 1,11-undecanediol.

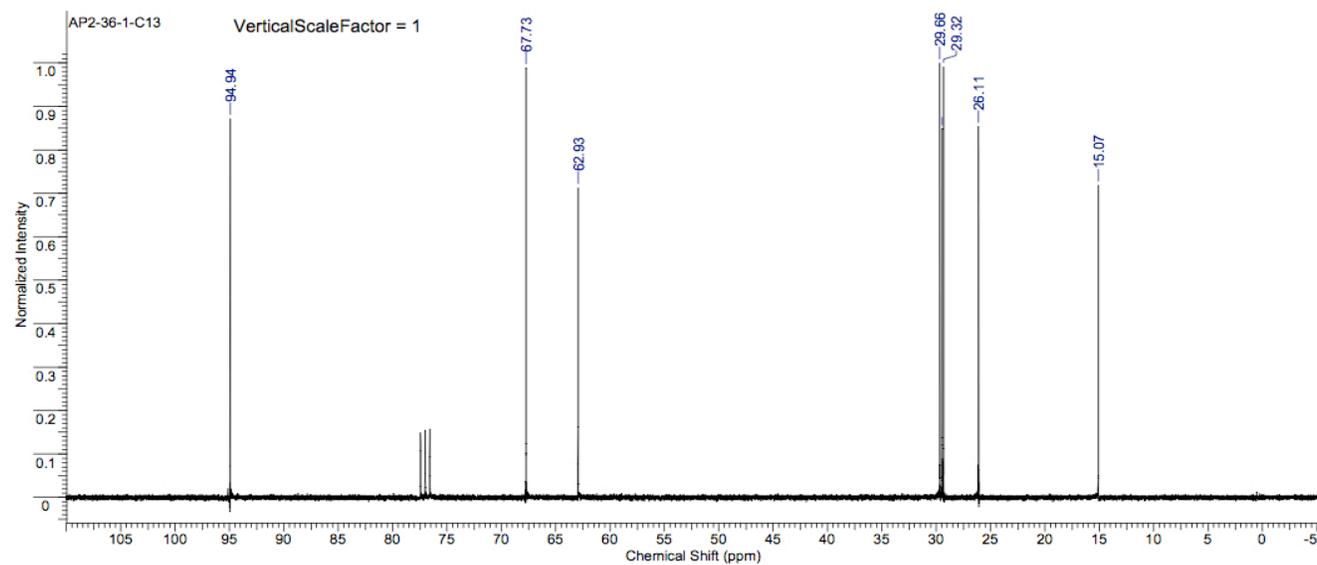


Figure S112. ¹³C NMR spectrum of 3,5,16,18-tetraoxaicosane.

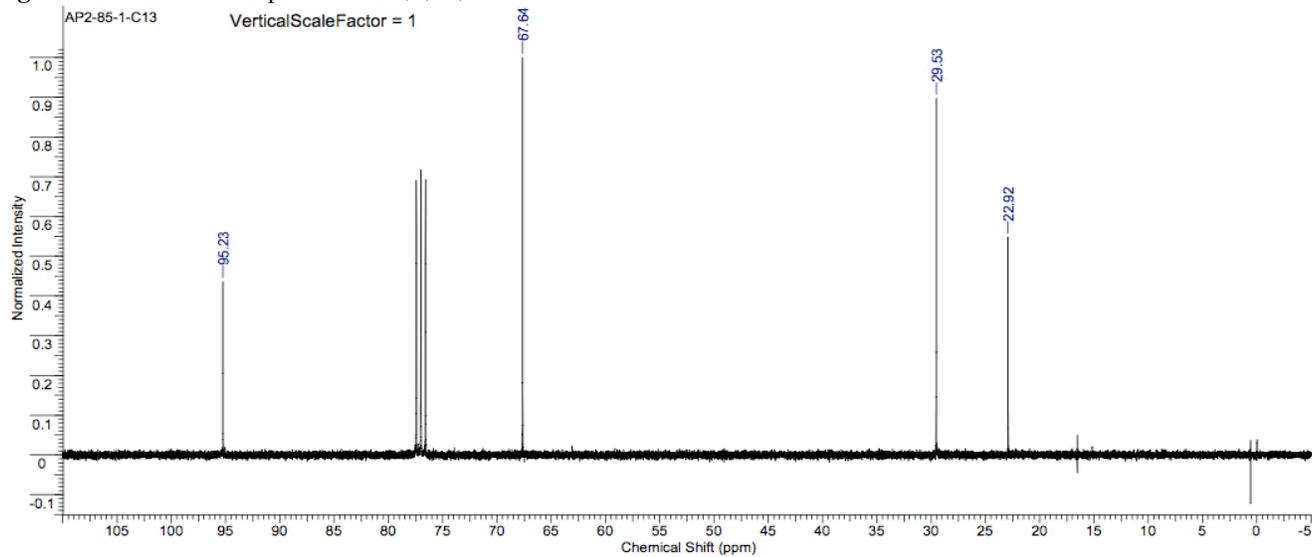


Figure S113. ¹³C NMR spectrum of polypentylene acetal (Table S1, entry 1).

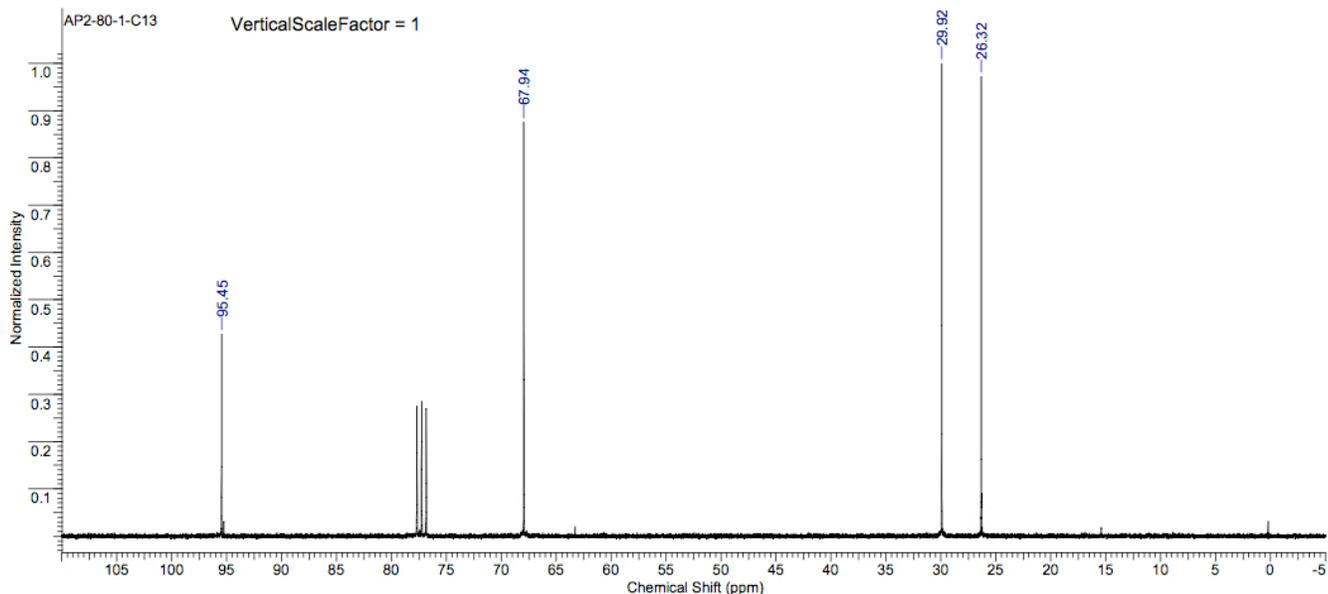


Figure S114. ^{13}C NMR spectrum of polyhexylene acetal (Table S1, entry 2).

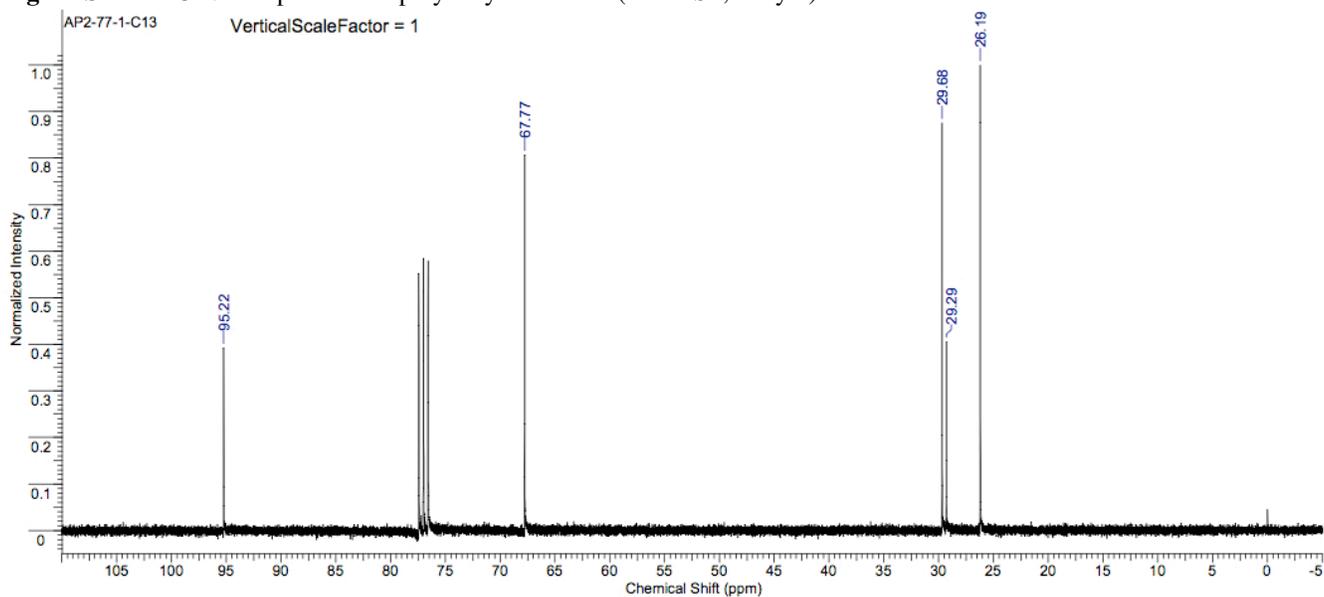


Figure S115. ^{13}C NMR spectrum of polyheptylene acetal (Table S1, entry 3).

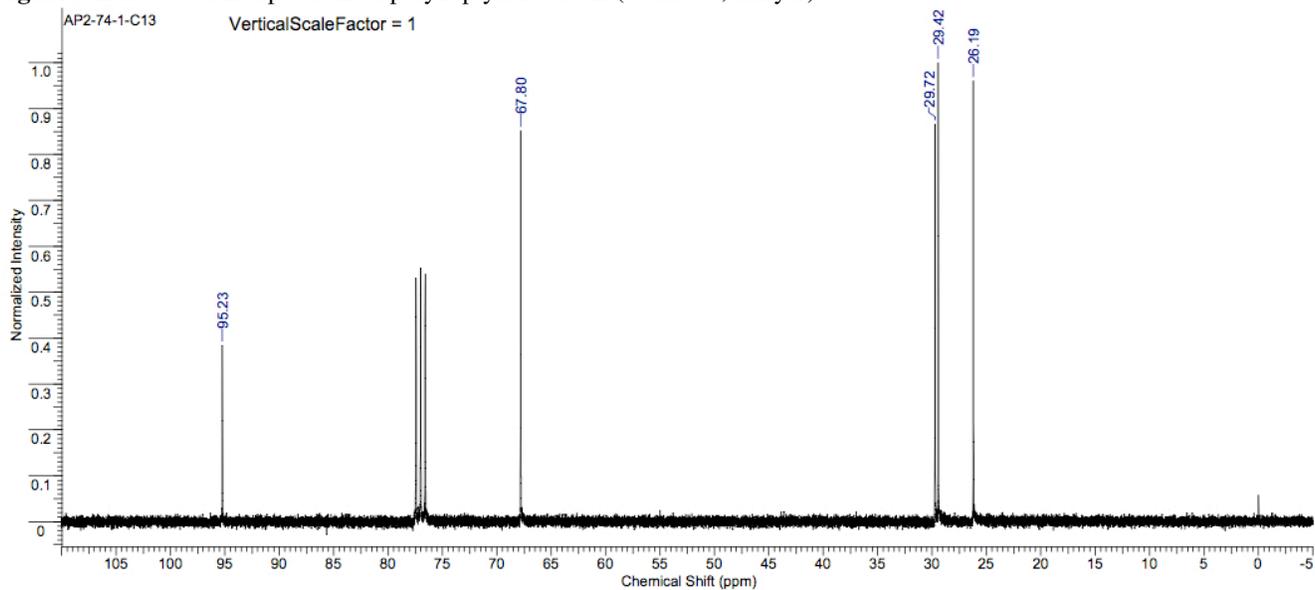


Figure S116. ^{13}C NMR spectrum of polyoctylene acetal (Table S1, entry 4).

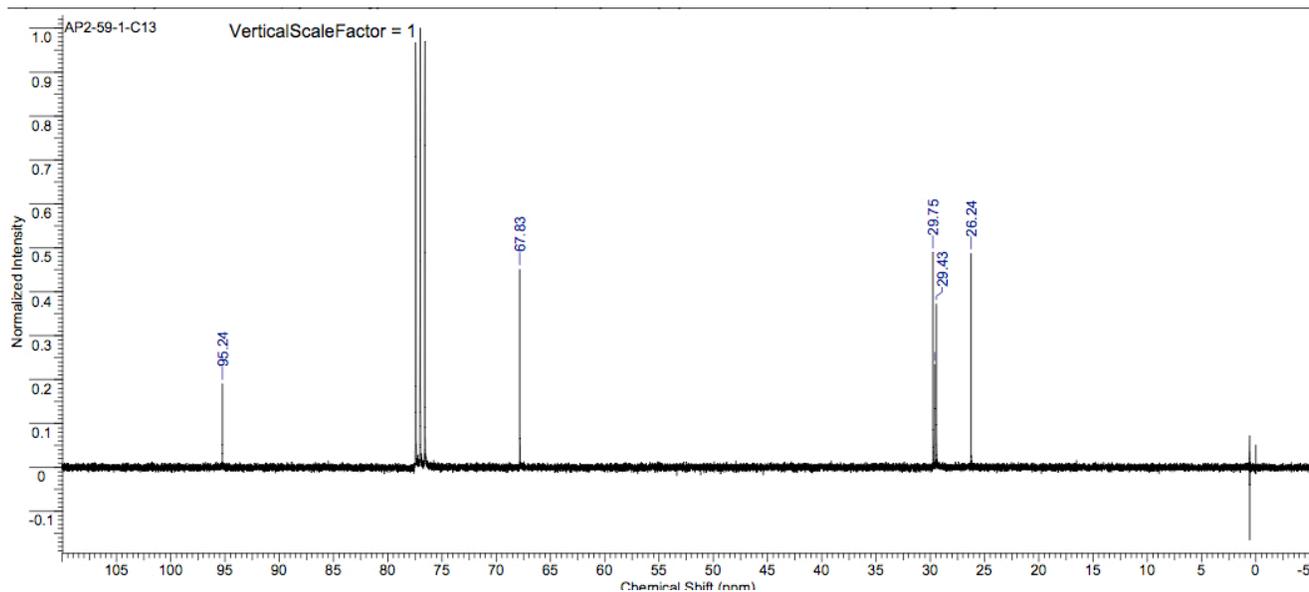


Figure S117. ¹³C NMR spectrum of polynonylene acetal (Table S1, entry 5).

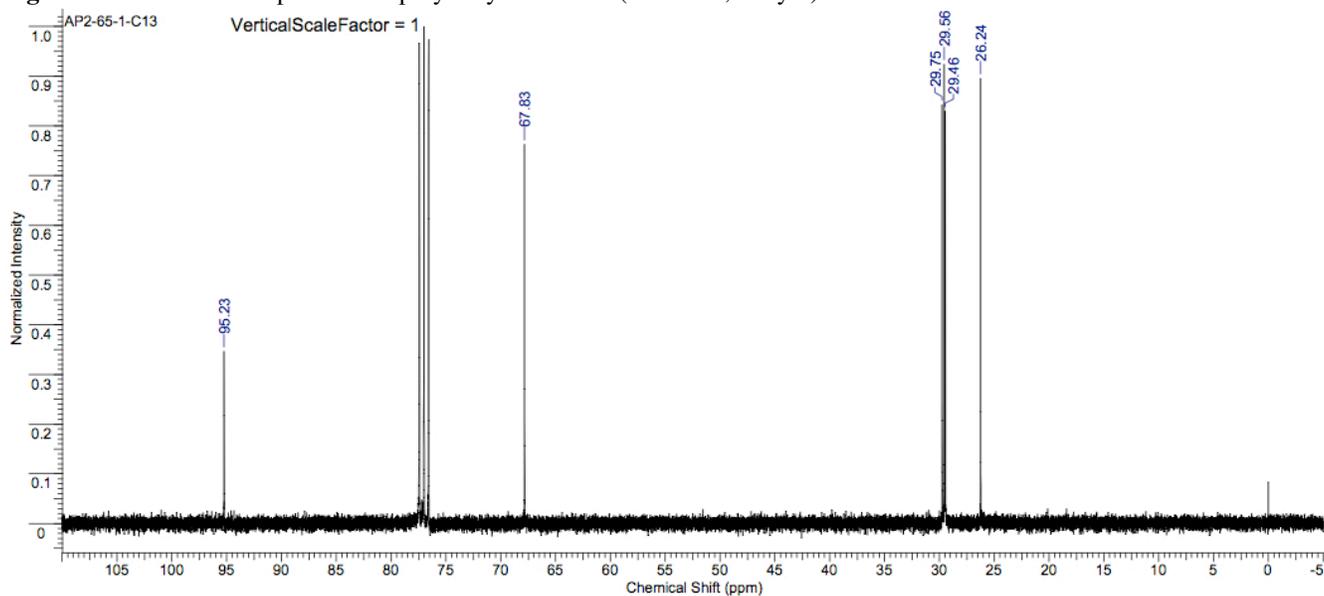


Figure S118. ¹³C NMR spectrum of polydecylene acetal (Table S1, entry 6).

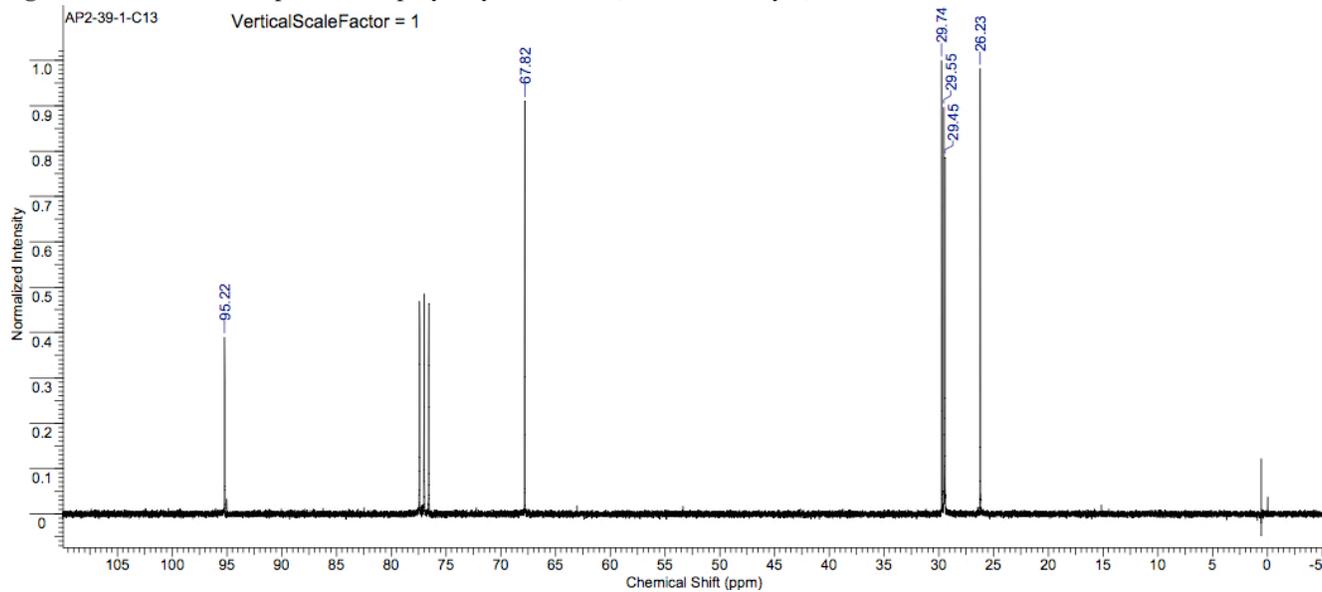


Figure S119. ¹³C NMR spectrum of polydecylene acetal, from the two-pot synthesis (Table S1, entry 7).

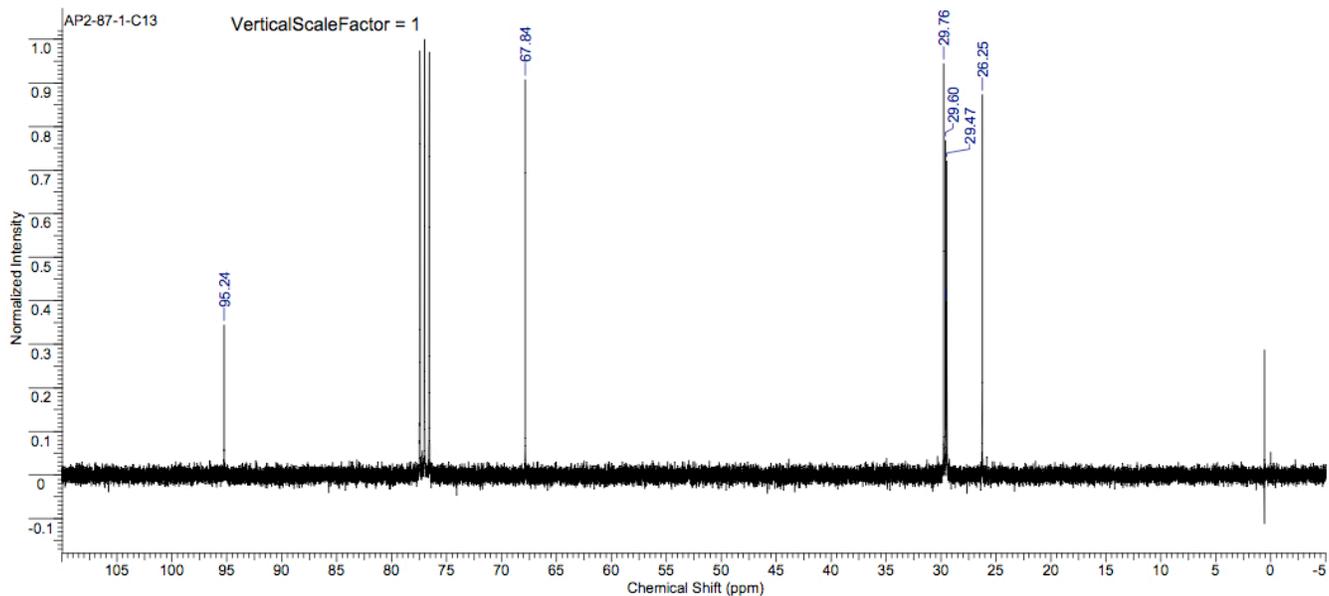


Figure S120. ^{13}C NMR spectrum of polyundecylene acetal (Table S1, entry 8).

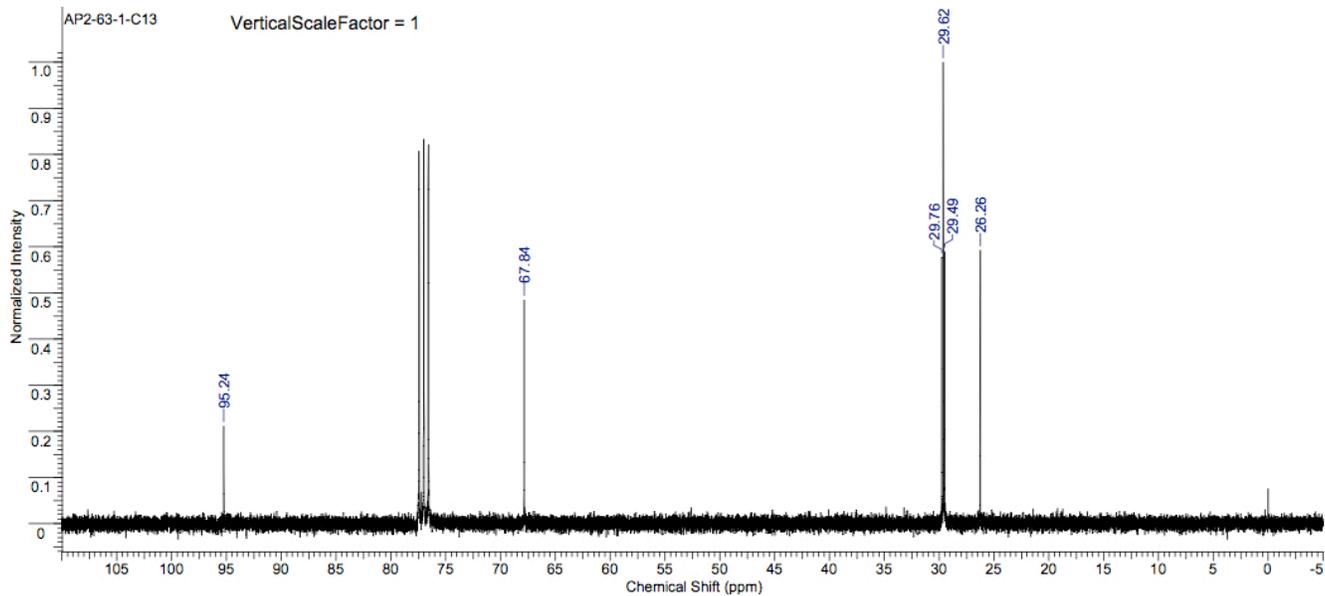


Figure S121. ^{13}C NMR spectrum of polydodecylene acetal (Table S1, entry 9).

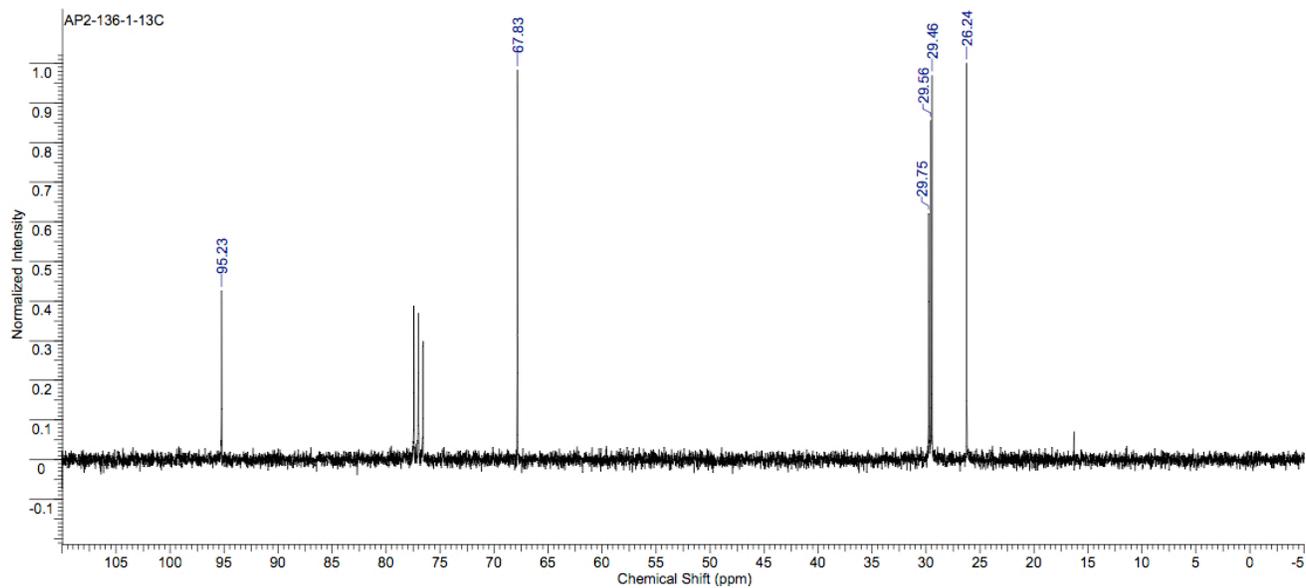


Figure S122. ^{13}C NMR spectrum of polydecylene acetal, *10 gram scale-up* (Table S1, entry 10).

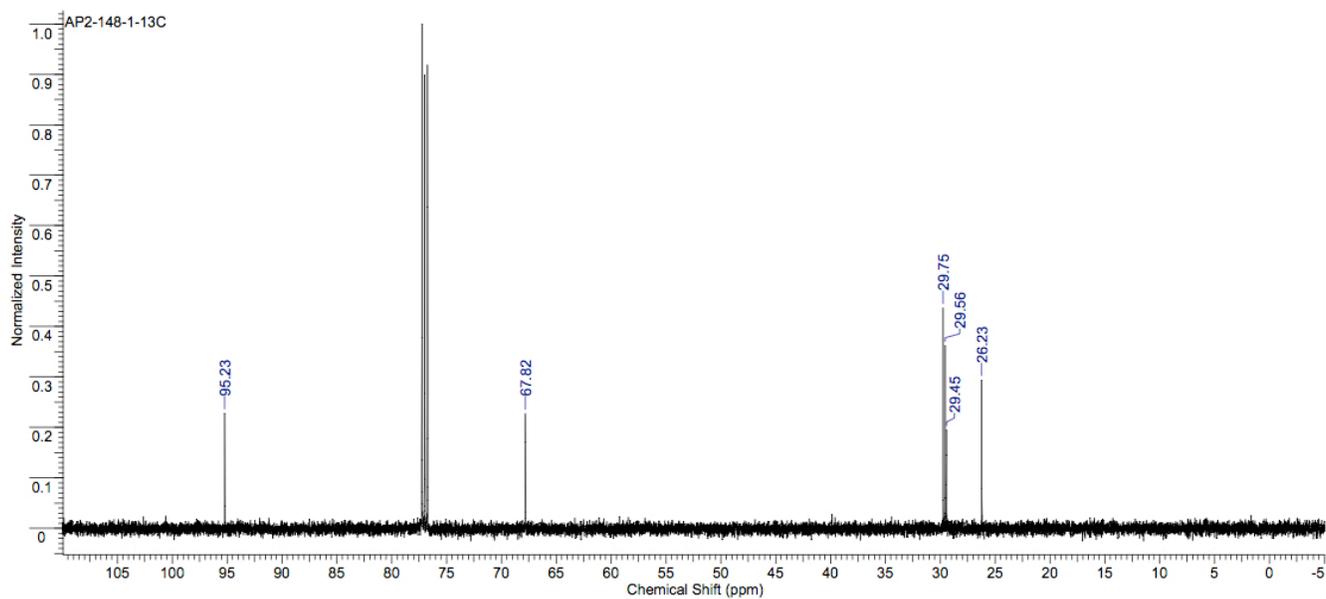


Figure S123. ^{13}C NMR spectrum of polydecylene acetal, *50 gram scale-up* (Table S1, entry 11).

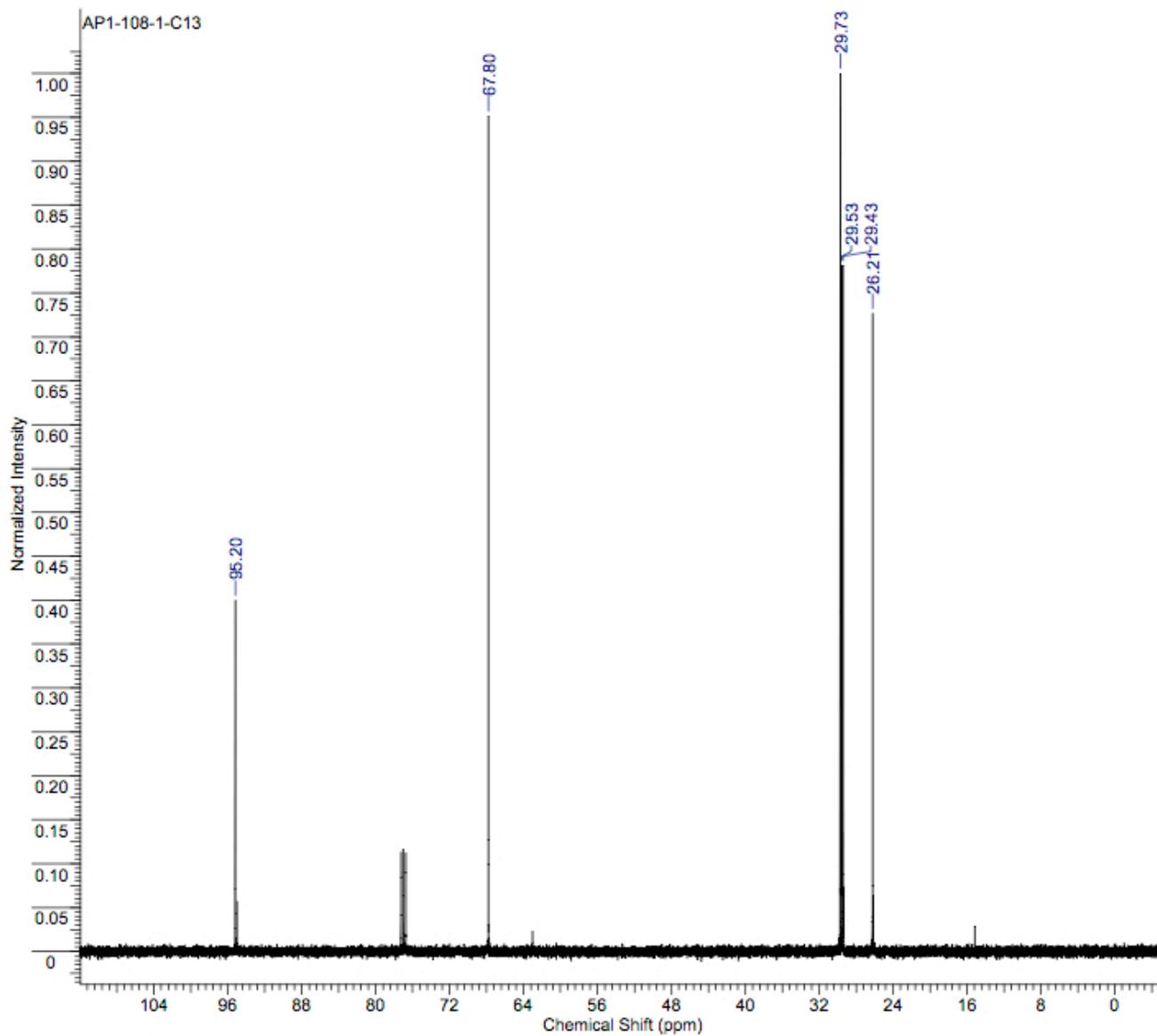


Figure S124. ^{13}C NMR spectrum of polydecylene acetal, *first iteration* (Table S1, entry 12).

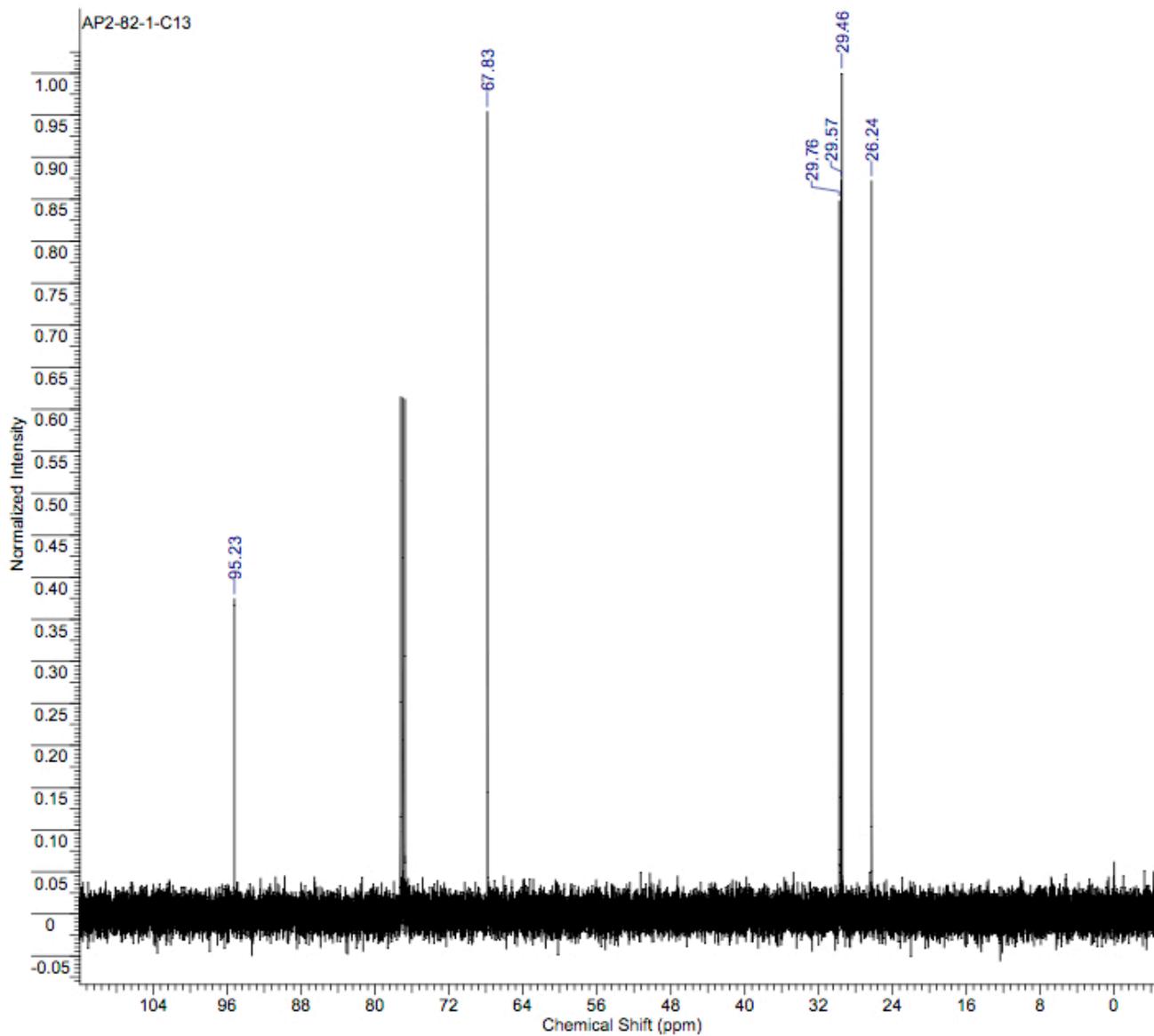


Figure S125. ^{13}C NMR spectrum of polydecylene acetal, *second iteration* (Table S1, entry 13).

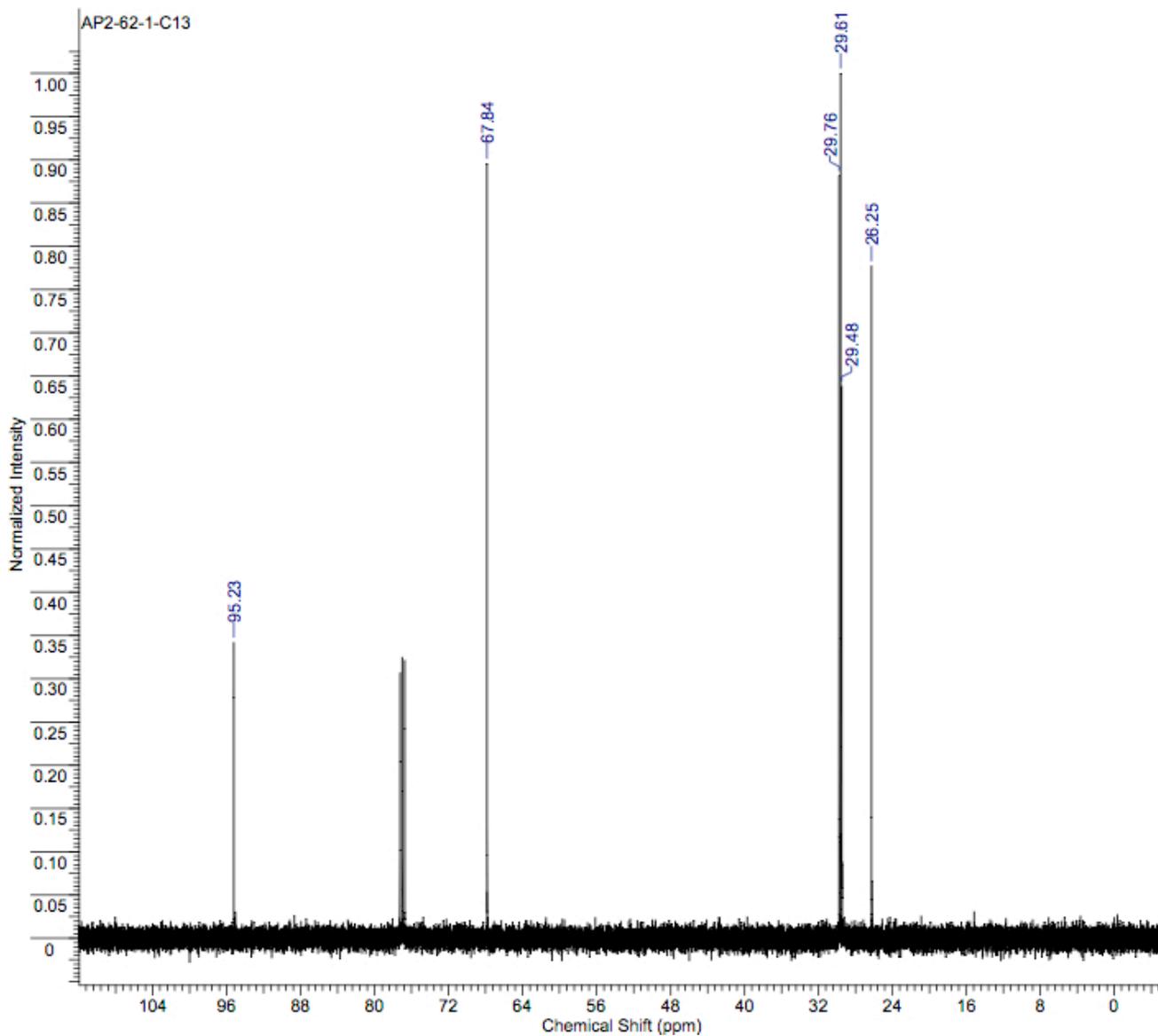


Figure S126. ¹³C NMR spectrum of polydodecylene acetal, *first iteration* (Table S1, entry 14).

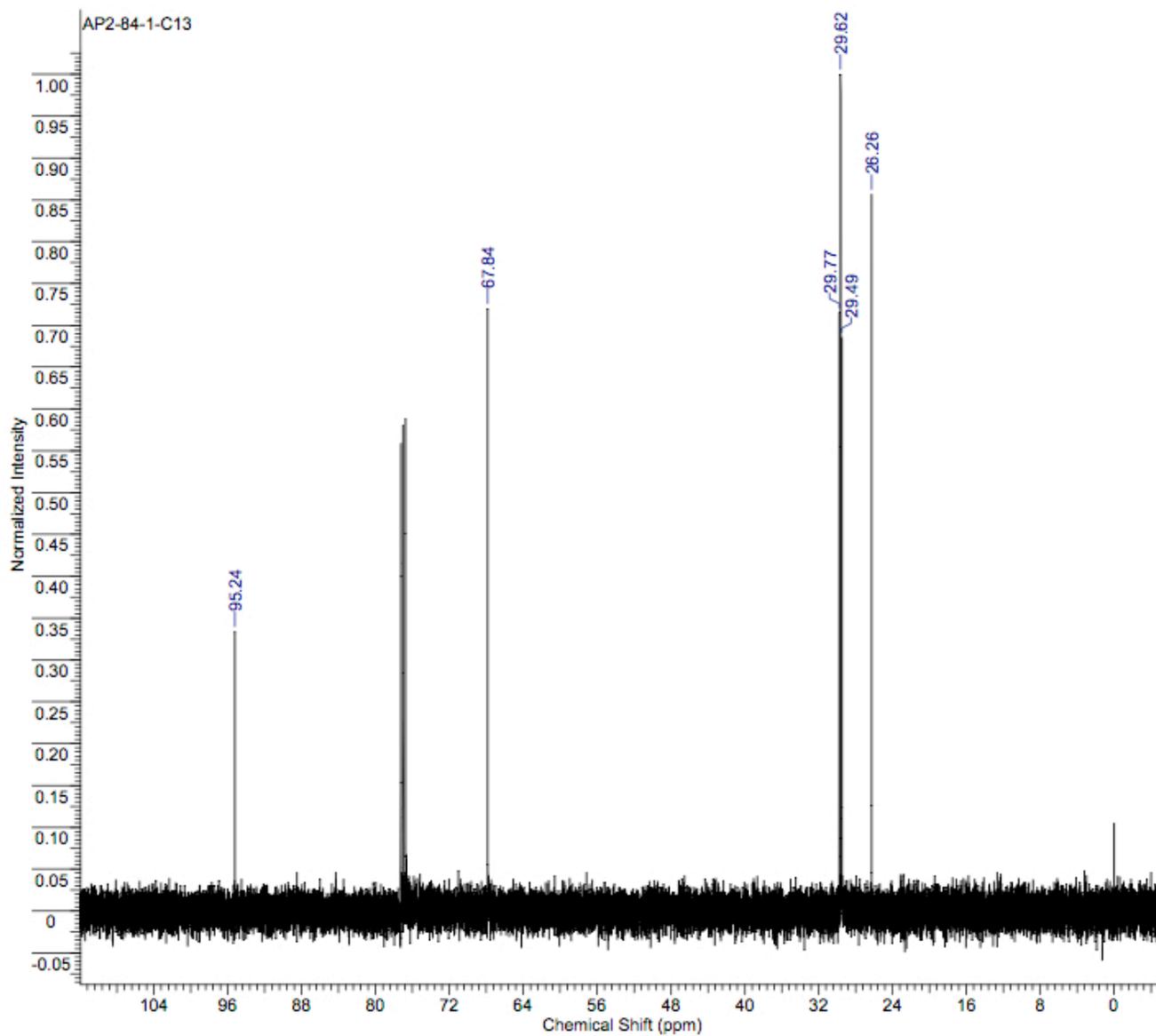


Figure S127. ^{13}C NMR spectrum of polydodecylene acetal, *second iteration* (Table S1, entry 15).

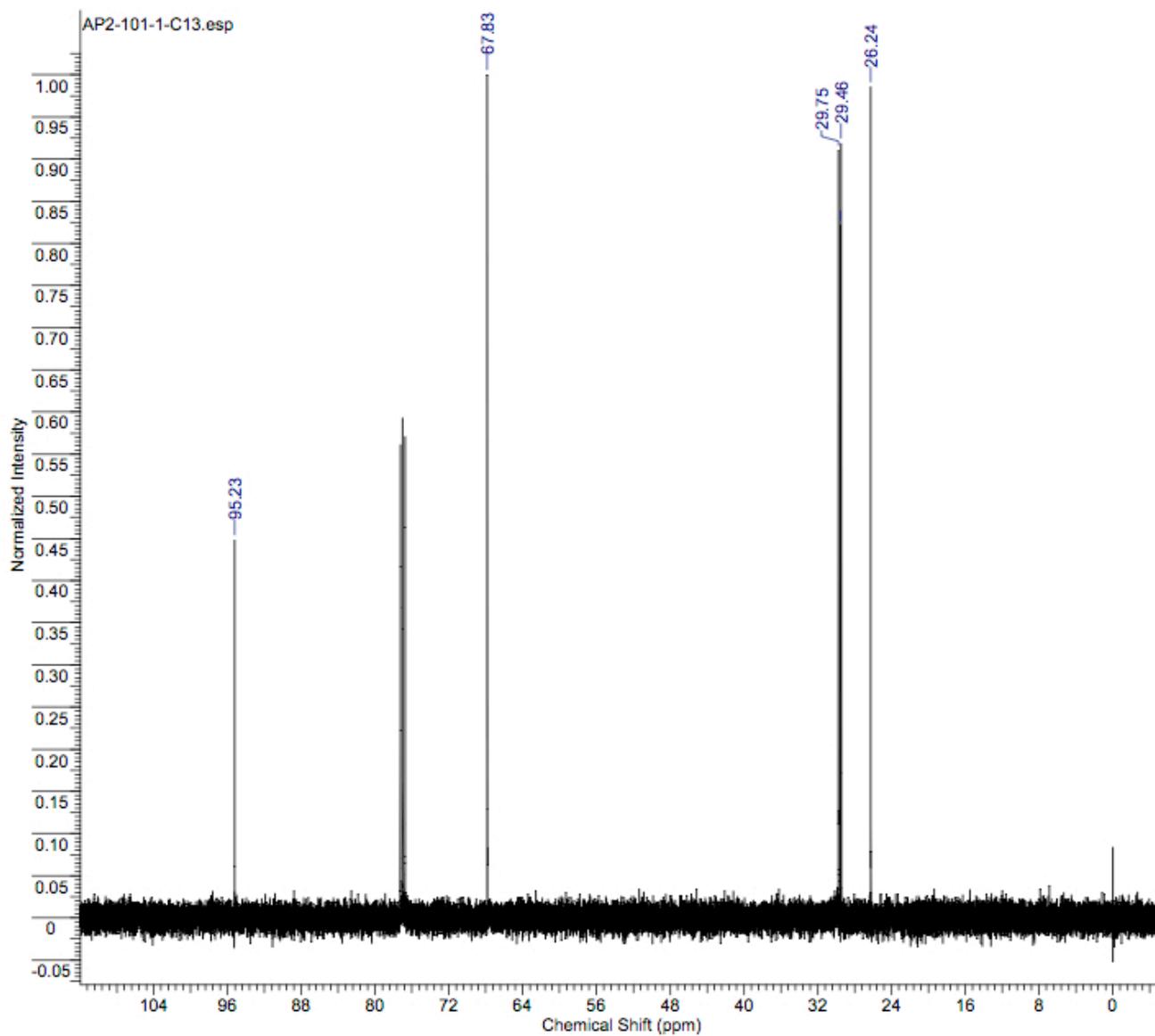


Figure S128. ^{13}C NMR spectrum of polydecylene acetal, from dimethoxymethane (Table S1, entry 16).

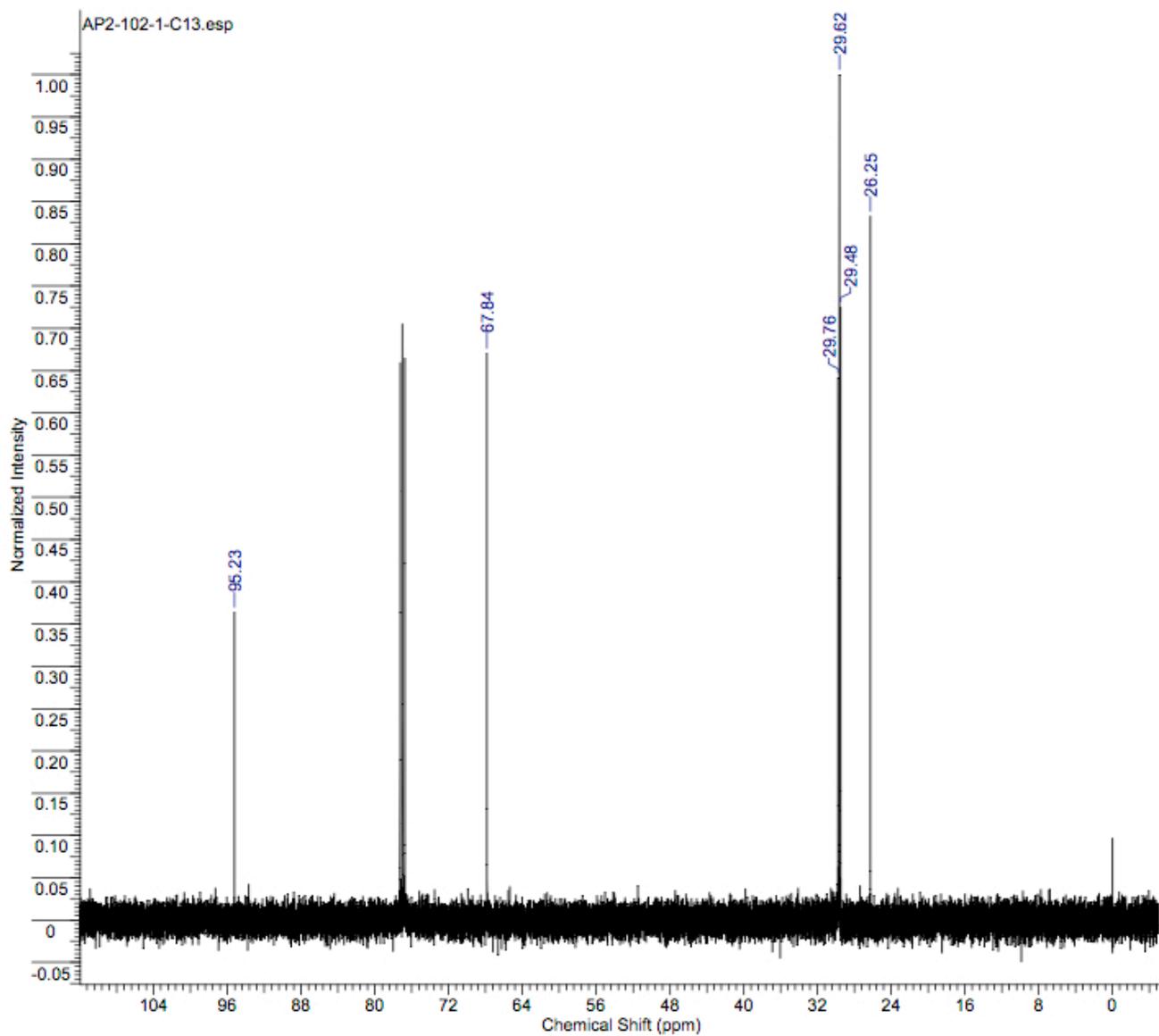


Figure S129. ^{13}C NMR spectrum of polydodecylene acetal, from dimethoxymethane (Table S1, entry 17).

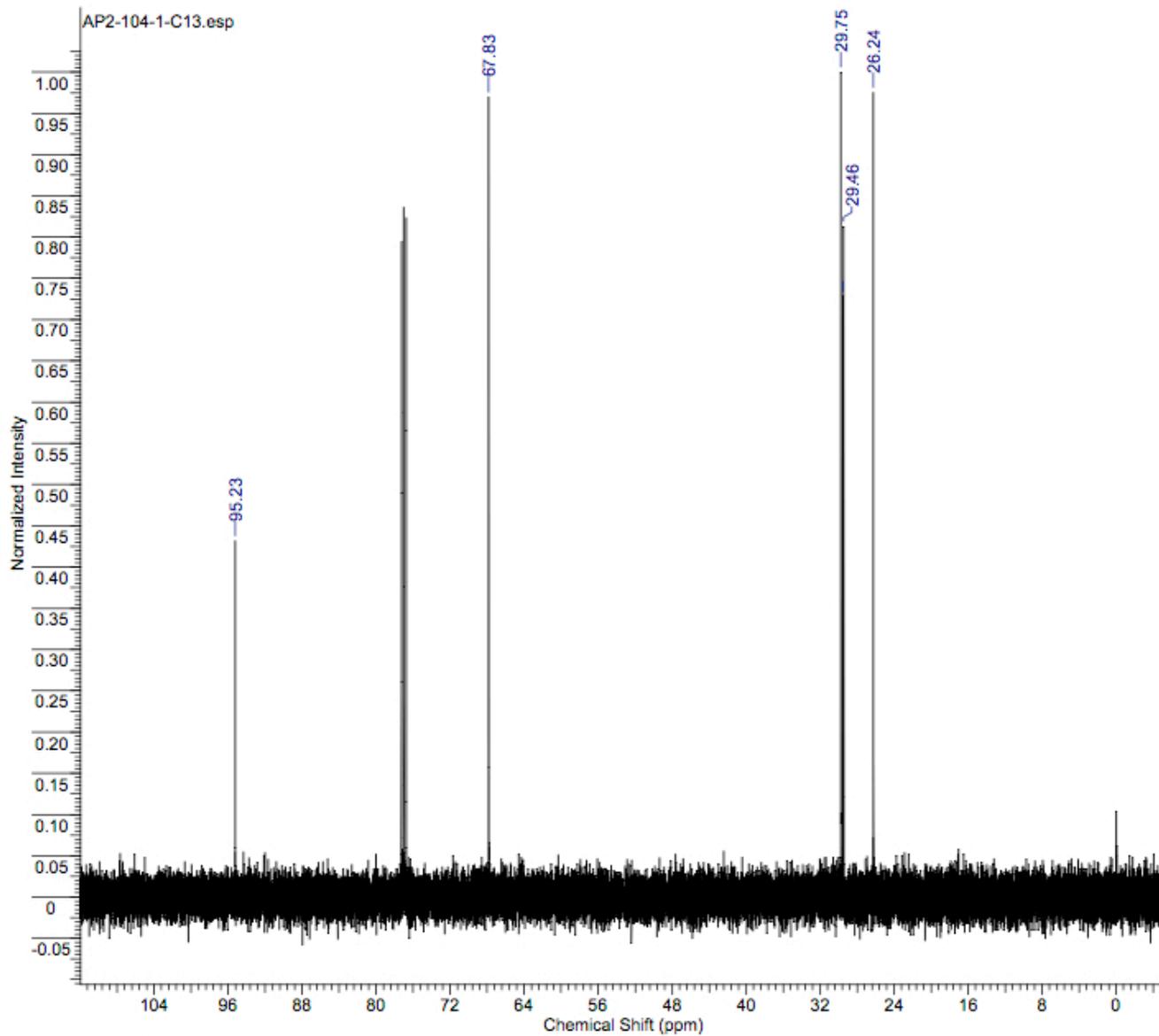


Figure S130. ^{13}C NMR spectrum of polydecylene acetal, from diethoxymethane:diol = 2:1 (Table S1, entry 18).

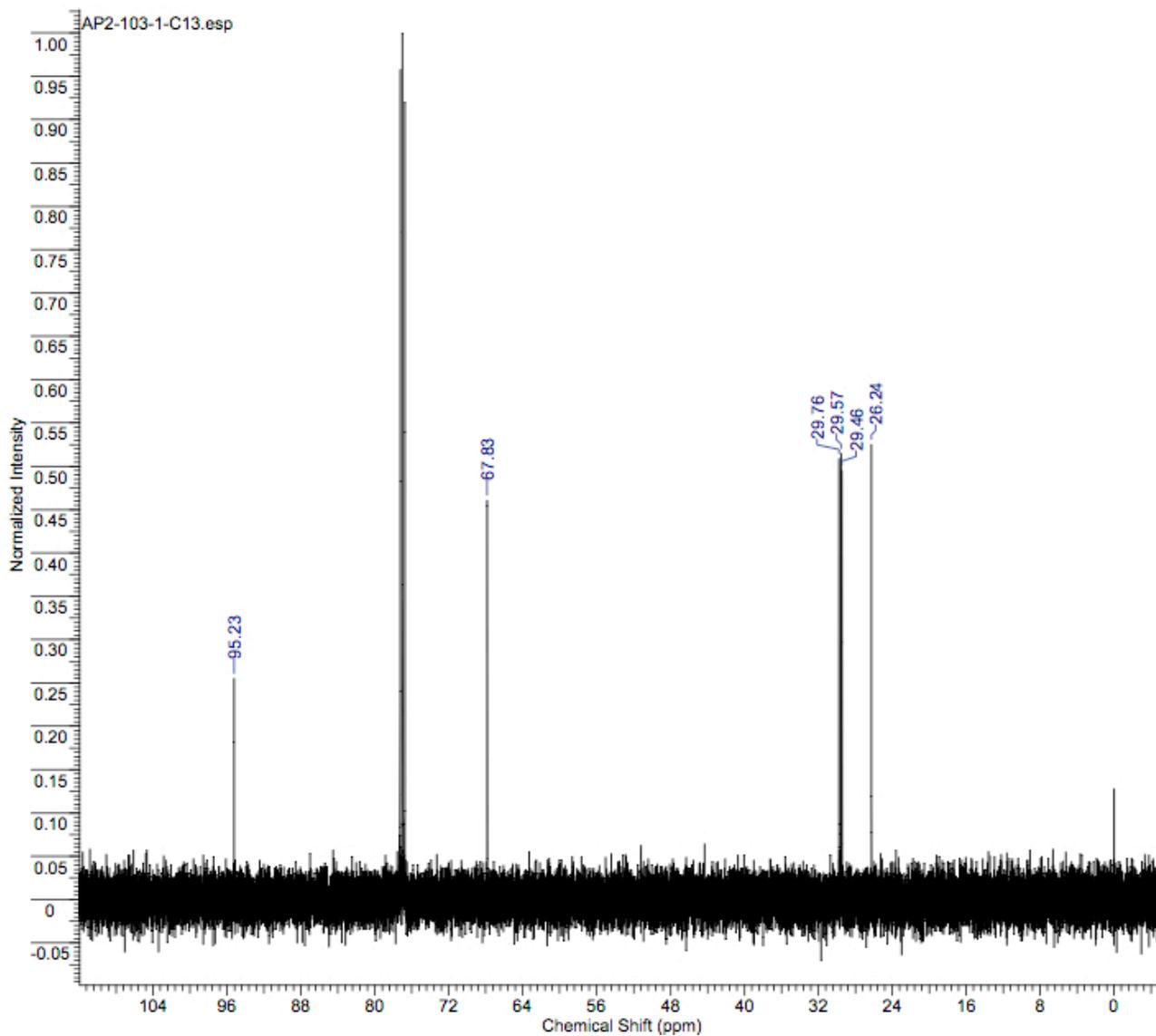


Figure S131. ^{13}C NMR spectrum of polydecylene acetal, from dimethoxymethane:diol = 2:1 (Table S1, entry 19).

References

- (1) Narasimhan, S.; Madhavan, S.; Prasad, K. G. *Synthetic Commun.* **1997**, *27*, 385–390.