13C NMR Spectroscopy for Quantitative Determination of Compound Ratios and Polymer End-Groups

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Supporting Information

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General Experimental Information:
All solvents were dried by filtration through alumina according to the method of Grubbs unless otherwise noted.1 Dichloromethane and 2-methyl-2-oxazoline were stirred over calcium hydride and distilled under argon prior to use. Ethanol was heated at reflux over sodium-benzophenone and distilled under argon prior to use. Methyl triflate was distilled prior to use. l-Lactide was recrystallized from toluene and stored under argon. All synthetic procedures were run under an atmosphere of nitrogen in glassware that was flame-dried under vacuum and cooled under a stream of nitrogen unless otherwise stated. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on silica gel (SiO2) 60 (230-400 mesh). 1H and 13C NMR spectra were acquired at ambient temperature using a BBO probehead on both the 400 and 500 MHz, and QXI probehead on the 600 MHz spectrometers, as indicated and were referenced to residual protio solvent.1 The proton 90 degree pulse widths for the 400, 500, and 600 MHz are 7.75, 9.95, and 9.8 μs, respectively. The carbon 90 degree pulse widths for the 400, 500, and 600 MHz are 11.4, 10.25, and 11.25 μs, respectively. The data are reported as follows: chemical shifts are reported in parts per million (δ), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, m = multiplet, app = apparent), coupling constants (J) in Hertz (Hz), and integration. Resonances in the 13C NMR spectra were assigned by HSQC data so the appropriate peaks can be compared. A Waltz-16 decoupling scheme with a pulse of 90 μsec was employed. Baseline correction was performed using the 5th order polynomial functions from -10 to 240 ppm range. MALDI-ToF spectra were acquired on a MALDI tandem mass spectrometer in positive ion mode. trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (for PLA and P(Ox)) or 1,8,9-anthracenetriol (dithranol) (for P(NO)) in THF was used as the matrix. A saturated sodium trifluoroacetate solution in acetone was spotted on top of the matrix layer as dopant salt and the compound of interest was applied in its respective deuterated solvent. For analysis, a “Synthetic Polymer Analysis Kit” was used to calculate degrees of polymerization from the mass peaks obtained. Infrared (IR) spectra were obtained using an FT-IR spectrometer. High resolution mass spectra (HRMS) were acquired on a time-of-flight spectrometer. Analytical gas chromatography (GC) was performed on a chromatograph equipped with an auto-sampler and flame-ionization detector. A fused silica capillary column (30 m x 0.320 mm x 0.25 mm) wall-coated with DB-1 was used with helium gas carrier (25 psi column head pressure). Unless otherwise noted, all reagents and substrates were commercially available.
General Information Related to the Processing of $^{13}$C NMR Spectra:
For the acquisition of $^{13}$C NMR spectra associated with molecules with similar connectivity (i.e.,
diastereomers) or for ratios greater than 9:1 (i.e., polymer end-group analysis with DP > 10),
broadband decoupled pulse programs were used. For the acquisition of $^{13}$C NMR spectra associated
with molecules of dissimilar connectivity (i.e., constitutional isomers, unrelated molecules, etc)
inverse-gated decoupled pulse programs were used. Relaxation delays were limited to either 2 sec
(short) or 30 sec (long) for comparison purposes, sweep width was set to 24k Hz on a 400 MHz
spectrometer, the total number of data points collected was 64k, and the number of scans varied from
16 to 8000 (512 was used most commonly). When processing data, line broadening (LB) was set to 0.0,
SI was set to 128k (2 x TD), and all mathematical fits employed during the deconvolution procedure
were 100% Lorentzian in nature. If LB is set to 0.0 and SI is not 2 x TD, peak widths at half-height of
0.0 may cause the deconvolution procedure to terminate prematurely. Note, end-group analysis of
polymers required line LB > 0 to improve signal to noise.

Synthetic Procedures:

2,3-Diphenylbutane-2,3-diol (1): Synthesis was performed according to a previously reported
literature procedure, and characterization data matched those reported in the literature.$^{2}$

2,5-Diphenylhexane-2,5-diol (2): Synthesis was performed according to a previously reported
literature procedure for the synthesis of 1$^{3}$, and characterization data matched those reported in the
literature.$^{4}$

2,6-Diphenylheptane-2,6-diol (3): Synthesis was performed according to a previously reported
literature procedure for the synthesis of 1$^{5}$. Crude diastereomeric mixture with residual EtOAc:
colorless oil; $^1$H (400 MHz, CDCl$_3$) $\delta$ 7.30 (m, 10H), 1.75 (m, 6H), 1.49 (s, 3H), 1.48 (s, 3H), 1.20 (m,
2H); $^{13}$C (400 MHz, CDCl$_3$) $\delta$ 148.125, 148.116, 128.26, 128.25, 126.64, 126.63, 124.81, 124.80, 74.8,
44.3, 44.2, 30.3, 30.1, 18.6, 18.5; IR (ATR) 3409, 2972 cm$^{-1}$; HRMS (TOF MS ES+) $m/z$ calcd for
C$_{19}$H$_{24}$O$_2$ [M + Na]$^+$ 307.1674, found 307.1679.
5,8,14,17-Tetraoctyloxy-2,11-dithia[3.3]paracyclophane and 6,9,14,17-tetraoctyloxy-2,11-dithia-[3.3]paracyclophane: Synthesis of the two regioisomers was performed according to a previously reported literature procedure and characterization data matched those reported in the literature.\textsuperscript{6}

\[
\begin{array}{c}
\text{R} = \text{C}_8\text{H}_{17} \\
\end{array}
\]

**Allyl lactide:** Synthesis was performed according to a previously reported literature procedure\textsuperscript{7} and characterization data matched those reported in the literature.\textsuperscript{8}

\[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{N} \\
\text{Me} \\
\text{O} \\
\text{O} \\
\end{array}
\]

**N-Benzyl-N-methylacetamide:** Synthesis was performed according to a previously reported literature procedure and characterization data matched those reported in the literature.\textsuperscript{9}

\[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{Et} \quad \text{OH} \\
\text{Me} \\
\end{array}
\]

**Poly(lactic acid) (P(LA)):** Synthesis was performed according to a previously reported literature procedure except that ethanol was used as the initiator.\textsuperscript{10}
Poly(4-methyl-oxazoline) (P(Ox)): Synthesis was performed according to a modified procedure previously reported in the literature. A representative procedure affording a polymer with DP = 10 is described. A stock solution of methyl triflate (0.200 mL, 1.83 mmol) in MeCN (1.8 mL) was prepared. To a Schlenk reactor under an atmosphere of argon was added 2-methyl-2-oxazoline (0.311 g, 3.66 mmol), chlorobenzene (0.300 mL), and methyl triflate stock solution (0.414 mL, 0.37 mmol). The reactor was then heated (70°C) in an oil bath. Per repeat unit monomer one hour of polymerization time was assumed, so that the polymerization reaction described was heated for ten hours. Water (ca. 1 mL) was added to terminate the polymerization and the reaction mixture was stirred for two hours. The mixture was concentrated in vacuo, yielding a yellow oil. The crude product was dissolved in CHCl₃ (0.5 mL) and precipitated into cold Et₂O. Following centrifugation at 4000 rpm for 20 minutes, the supernatant was decanted and the process repeated two additional times, affording the desired poly(4-methyl-oxazoline) (0.077 g, 25% yield) as a white solid.

Octyl (1R,2S,4R)-bicyclo[2.2.1]hept-5-ene-2-carboxylate: To a cooled (0°C) mixture of bicyclo[2.2.1]hept-5-ene-exo-2-carboxylic acid (norbornene exo acid) (1.5 g, 11 mmol), one spatula tip of 4-dimethylaminopyridine (DMAP), and n-octanol (2.23 mL, 14.1 mmol) in anhydrous CH₂Cl₂ (11 mL) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC, 2.71 g, 14.1 mmol) portion-wise. The mixture was allowed to warm to room temperature over 12 h before being diluted with CH₂Cl₂ (40 mL) and extracted with 0.5 N HCl (2 x 100 mL). The organic layers were combined, washed with saturated aqueous NaHCO₃ (100 mL), dried over magnesium sulfate, and concentrated in vacuo, yielding a yellow oil. Purification by silica gel column chromatography (9:1 hexanes:EtOAc) afforded the desired product (2.28 g, 84% yield) as a clear oil. Analytical data were in accordance with the literature.

Poly(norbornene octanoate) (P(NO)): Synthesis was performed according to a modified procedure previously reported in the literature. In two separate Schlenk reactors under an atmosphere of argon, exo-norbornene octanoate (0.300 g, 1.19 mmol) was dissolved in anhydrous CH₂Cl₂ (5 mL), and Grubbs 1st generation catalyst (0.098 g, 0.12 mmol) was dissolved in anhydrous CH₂Cl₂ (1 mL). The dissolved Grubbs 1st generation catalyst was transferred to the Schlenk reactor containing exo-norbornene octanoate using a syringe. The reaction mixture was stirred for 5 min. before an excess of ethyl vinyl ether (1 mL) was added to terminate the polymerization. After stirring for one hour, the mixture was concentrated in vacuo, yielding a black oil. Purification by preparative thin layer chromatography on silica (1:80 MeOH:CH₂Cl₂; 50 mg crude product per plate) afforded the desired product (0.222 g, 74% yield) as a light brown oil. Analytical data were in accordance with the literature, yet with a methylene end-group rather than a cyanuric acid.
References:

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NMR Spectra:

Spectrum S-1: $^1$H NMR spectrum of 1 from Scheme 1.
Spectrum S-2: $^{13}$C NMR spectrum of $\text{1}$ from Scheme 1.
Spectrum S-3: $^1$H NMR spectrum of 2 from Scheme 1 and Table 1.
Spectrum S-4: $^1$H NMR spectrum of 2 from Scheme 1 and Table 1.
Spectrum S-5: Crude $^1$H NMR spectrum of 3 from Scheme 1.
Spectrum S-6: Crude $^{13}$C NMR spectrum of 3 from Scheme 1.
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Spectrum S-7: Deconvoluted crude $^{13}$C NMR spectrum of 3 from Scheme 1.
Spectrum S-8: $^1$H NMR spectrum of camphor:fenchone (mol % fenchone = 39.2%) from Table 2.
Spectrum S-9: $^{13}$C NMR spectrum of camphor:fenchone (mol % fenchone = 39.2%) from Table 2.
Spectrum S-10: Deconvoluted $^{13}$C NMR spectrum of camphor:fenchone (mol % fenchone = 39.2%) from Table 2. See Table SI-2 for tabulated integrals.
Spectrum S-11: Single-pulse $^1$H NMR spectrum of camphor:fenchone (mol % fenchone = 39.2%) from Figure 1.
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Spectrum S-12: 128-Scan 1H NMR spectrum of camphor:fenchone (mol % fenchone = 39.2%) from Figure 1.
Spectrum S-13: BBD 13C NMR spectrum of camphor:fenchone (mol% fenchone=39.2%) from Figure 1.
Spectrum S-14: IGD $^{13}$C NMR spectrum of camphor:fenchone (mol % fenchone=39.2%) from Figure 1.
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Spectrum S-15: $^1$H NMR spectrum from Table 3.
Supporting Information: Otte, Borchmann, Lin, Weck, and Woerpel

Spectrum S-16: $^{13}$C NMR spectrum from Table 3.

Me
Me
Me OH

$E$- and $Z$-isomers
Supporting Information: Otte, Borchmann, Lin, Weck, and Woerpel

Spectrum S-17: 1H NMR spectrum from Table 3.

Current Data Parameters
NAME       DALO-V-91R
EXPN0      1
PROCNO     1

F2 - Acquisition Parameters
Date_      20131021
Time       14.31
INSTRUM    spect
PROBHD     5 mm PABBO BB/
PULPROG    zg30
TD          65536
SOLVENT    CDCl3
NS          1
DS          0
SWH         5597.015 Hz
FIDRES     0.085404 Hz
AQ          5.8545995 sec
RG          87.49
DW          89.333 usec
DE          6.50 usec
TE          298.1 K
DI          30.00000000 sec
TDO         1

---------- CHANNEL f1 ----------
SF01        400.2224013 MHz
NUC1        1H
F1          16.00 usec
PLW1        12.00000000 W

F2 - Processing parameters
ST          65536
SF          400.2200070 MHz
WDW         EM
SSB         0
LB          0 Hz
GB          0
PC          1.00
Spectrum S-18: 13C NMR spectrum from Table 3.
Supporting Information: Otte, Borchmann, Lin, Weck, and Woerpel

Spectrum S-19: $^1$H NMR spectrum from Table 3.
Spectrum S-20: $^{13}$C NMR spectrum from Table 3.
Spectrum S-21: 1H NMR spectrum from Table 3.
Supporting Information: Otte, Borchmann, Lin, Weck, and Woerpel

Spectrum S-22: $^13$C NMR spectrum from Table 3.

OH Me
Me OH
Me

Current Data Parameters
NAME DALO-V-111R
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20131028
Time 4.51
IMSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgi30
TD 65536
SOLVENT CDC13
NS 512
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 200.67
DW 20.800 usec
DE 6.50 usec
TE 298.1 K
D1 30.0000000 sec
d11 0.03000000 sec
d0 1
NUC1 13C
P1 9.75 usec
PLW1 54.00000000 W
SFO1 100.6469721 MHz
CPDPRG2
NUC2 1H
PLW2 12.00000000 W
PLW12 0.37926000 W
SFO2 400.2216009 MHz

F2 - Processing parameters
SI 131072
SP 100.6353877 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.40
Spectrum S-23: $^1$H NMR spectrum from Table 3.
Spectrum S-24: $^{13}$C NMR spectrum from Table 3.
Supporting Information: Otte, Borchmann, Lin, Weck, and Woerpel

Spectrum S-25: 1H NMR spectrum from Table 3.
Spectrum S-26: $^{13}$C NMR spectrum from Table 3.
Spectrum S-27: $^1$H NMR spectrum from Table 4.
Supporting Information: Otte, Borchmann, Lin, Weck, and Woerpel

Spectrum S-28: 13C NMR spectrum from Table 4.
Spectrum S-30: $^{13}$C NMR spectrum from Table 4.
Spectrum S-31: $^1$H NMR spectrum from Table 4.
Supporting Information: Otte, Borchmann, Lin, Weck, and Woerpel

Spectrum S-32: 13C NMR spectrum from Table 4.
Supporting Information: Otte, Borchmann, Lin, Weck, and Woerpel

Spectrum S-33: 1H NMR spectrum from Table 4.
Supporting Information: Otte, Borchmann, Lin, Weck, and Woerpel

Spectrum S-34: 13C NMR spectrum from Table 4.
Spectrum S-35: $^1$H NMR spectrum from Table 5.
Supporting Information: Otte, Borchmann, Lin, Weck, and Woerpel

Spectrum S-36: 13C NMR spectrum from Table 5.
Spectrum S-37: $^1$H NMR spectrum from Table 6.
Spectrum S-38: $^{13}$C NMR spectrum from Table 6.

Current Data Parameters
NAME   DB5-69-10-2
EXPN0  1
PROCNO 1

F2 - Acquisition Parameters
Date   20130925
Time   21.42
INSTRUM spect
PROBH0 5 mm PABBO BS/
PULPROG zgptq30
TD     65536
SOLVENT CDC13
NS     112
DS     4
SWR    24038.461 Hz
FIDRES 0.364798 Hz
AQ     1.3631988 sec
RG     200.67
DW     20.800 usec
DE     6.50 usec
TE     298.1 K
D1     2.0000000 sec
d11    0.03000000 sec
DELTA  1.89999998 sec
TD0    1
NUC1  13C
P1     9.75 usec
PLW1   54.00000000 W
SF01   100.6469721 MHz
CQDRG2
NUC2   1H
PLW2   12.00000000 W
PLW12  0.37926000 W
PLW13  0.30720001 W
SF02   400.2216009 MHz

F2 - Processing parameters
SI     131072
SF     100.6353862 MHz
WDW    EM
SSB    0
LB     0 Hz
GB     0
PC     1.40
Spectrum S-39: $^1$H NMR spectrum from Table 6.
Spectrum S-40: $^{13}$C NMR spectrum from Table 6.
Spectrum S-41: 1H NMR spectrum of 10-mer from Table 6.
Supporting Information: Otte, Borchmann, Lin, Weck, and Woelpel

Spectrum S-42: $^{13}$C NMR spectrum of 10-mer from Table 6.

Current Data Parameters
NAME: DBS-112-1-2
EXPNO: 1
PROCNO: 1

F2 - Acquisition Parameters
Date: 20131104
Time: 10.04
INSTRUM: spect
PROBHD: 5 mm PABBO BB/
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NS: 512
DS: 4
SWH: 24038.461 Hz
FIDRES: 0.366798 Hz
AQ: 1.3631988 sec
RG: 200.67
DW: 20.800 usec
DE: 6.50 usec
TE: 298.1 K
D1: 2.0000000 sec
d1: 0.03000000 sec
DELTAD: 1.89999998 sec
TD0: 1
NUC1: 13C
pl: 9.75 usec
PLW1: 54.0000000 W
SFQ1: 100.6469721 MHz
CPDPRG2
NUC2: 1H
PLW2: 12.00000000 W
PLW3: 12.00000000 W
PLW13: 0.307200001 W
SFQ2: 400.2216009 MHz

F2 - Processing parameters
SI: 131072
SF: 100.6353931 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 1.40
Spectrum S-43: $^1$H NMR spectrum of 15-mer from Table 6.
Supporting Information: Otte, Borchmann, Lin, Weck, and Woerpel

Spectrum S-44: $^{13}$C NMR spectrum of 15-mer from Table 6.
Spectrum S-45: $^1$H NMR spectrum from Table 6.
Spectrum S-46: $^{13}$C NMR spectrum from Table 6.
Tables of Deconvolution Data:

General: $^{13}$C NMR spectra of polymers were acquired using BBD acquisition with $D_1 = 2$ sec and at least 512 scans (in cases of complex polymer structures, 8192 scans are recommended).

Table SI-1. Deconvolution results for the $^{13}$C NMR spectrum* of 2 from Scheme 1.

| Peak chemical shift ($\delta$ ppm) | Peak Integral | Peak Assignment     |
|-----------------------------------|---------------|---------------------|
| 148.0                             | 0.60          | Major Diastereomer  |
| 147.7                             | 0.40          | Minor Diastereomer  |
| 128.3                             | 4.61          | Both Diastereomers  |
| 126.64                            | 1.23          | Minor Diastereomer  |
| 126.58                            | 0.92          | Minor Diastereomer  |
| 125.0                             | 1.86          | Minor Diastereomer  |
| 124.9                             | 2.45          | Major Diastereomer  |
| 74.6                              | 0.79          | Minor Diastereomer  |
| 74.5                              | 0.97          | Major Diastereomer  |
| 38.2                              | 1.30          | Major Diastereomer  |
| 38.1                              | 1.02          | Minor Diastereomer  |
| 31.4                              | 0.85          | Minor Diastereomer  |
| 30.6                              | 1.05          | Major Diastereomer  |

*BBD, 64 scans, $D_1 = 2$ sec

Table SI-2. Deconvolution results for the $^{13}$C NMR spectrum* of fenchone:camphor (39.2 mol% fenchone) sample from Table 2.

| Peak chemical shift ($\delta$ ppm) | Peak Integral | Peak Assignment |
|-----------------------------------|---------------|-----------------|
| Not Found                         | N/A           | Fenchone        |
| 219.9                             | 0.81          | Camphor         |
| 57.9                              | 1.00          | Camphor         |
| 54.3                              | 0.77          | Fenchone        |
| 47.5                              | 0.61          | Fenchone        |
| 46.9                              | 0.88          | Camphor         |
| 45.5                              | 1.85          | Fenchone        |
| 43.5                              | 3.07          | Camphor         |
| 43.2                              | 2.89          | Camphor         |
| 41.8                              | 1.80          | Fenchone        |
| 32.0                              | 1.96          | Fenchone        |
| 30.1                              | 2.99          | Camphor         |
| 27.2                              | 3.12          | Camphor         |
| 25.1                              | 2.10          | Fenchone        |
| 23.5                              | 1.59          | Fenchone        |
| 21.8                              | 1.97          | Fenchone        |
| 19.9                              | 2.86          | Camphor         |
| 19.3                              | 2.88          | Camphor         |
| 14.8                              | 1.69          | Fenchone        |
| 9.4                               | 2.42          | Camphor         |

*IGD, 16 scans, $D_1 = 2$ sec. See Spectrum S-9 for deconvoluted $^{13}$C NMR spectrum.
Table SI-3. Deconvolution results for the $^{13}$C NMR spectrum* of Nerol:Geraniol mixture from Table 3.

| Peak chemical shift ($\delta$ ppm) | Peak Integral | Peak Assignment |
|-----------------------------------|---------------|-----------------|
| 140.1                             | 1.57          | Nerol           |
| 139.9                             | 1.01          | Geraniol        |
| 132.6                             | 1.65          | Nerol           |
| 131.9                             | 0.98          | Geraniol        |
| 124.6                             | 1.36          | Nerol           |
| 124.02                            | 0.86          | Geraniol        |
| 123.95                            | 1.51          | Nerol           |
| 123.5                             | 0.92          | Geraniol        |
| 59.5                              | 0.85          | Geraniol        |
| 59.1                              | 1.47          | Nerol           |
| 39.7                              | 0.89          | Geraniol        |
| 32.1                              | 1.44          | Nerol           |
| 26.7                              | 1.48          | Nerol           |
| 26.5                              | 0.87          | Geraniol        |
| 25.81                             | 1.05          | Geraniol        |
| 25.79                             | 1.43          | Nerol           |
| 23.6                              | 1.53          | Nerol           |
| 17.82                             | 1.09          | Geraniol        |
| 17.79                             | 1.53          | Nerol           |
| 16.4                              | 1.00          | Geraniol        |

*IGD, 512 scans, D1 = 30 sec
Table SI-4. Deconvolution results for the $^{13}$C NMR spectrum* of 1,8-Cineole:L-Menthol mixture from Table 3.

| Peak chemical shift (δ ppm) | Peak Integral | Peak Assignment |
|----------------------------|---------------|----------------|
| 73.8                       | 1.66          | Cineole        |
| 71.7                       | 1.03          | Menthol        |
| 69.9                       | 1.89          | Cineole        |
| 50.3                       | 0.99          | Menthol        |
| 45.2                       | 0.97          | Menthol        |
| 34.7                       | 0.98          | Menthol        |
| 33.1                       | 1.60          | Cineole        |
| 31.8                       | 1.03          | Menthol        |
| 31.6                       | 3.14          | Cineole        |
| 29.0                       | 2.94          | Cineole        |
| 27.7                       | 1.44          | Cineole        |
| 26.0                       | 0.93          | Menthol        |
| 23.3                       | 0.95          | Menthol        |
| 23.0                       | 3.18          | Cineole        |
| 22.4                       | 0.94          | Menthol        |
| 21.2                       | 1.00          | Menthol        |
| 16.3                       | 1.00          | Menthol        |

*IGD, 512 scans, D1 = 30 sec

Table SI-5. Deconvolution results for the $^{13}$C NMR spectrum* of L-(-)-Carvone:(+)-Limonene mixture from Table 3.

| Peak chemical shift (δ ppm) | Peak Integral | Peak Assignment |
|-----------------------------|---------------|----------------|
| 199.9                       | 0.97          | Carvone        |
| 150.4                       | 0.57          | Limonene       |
| 146.8                       | 1.02          | Carvone        |
| 144.7                       | 0.92          | Carvone        |
| 135.6                       | 1.04          | Carvone        |
| 133.9                       | 0.61          | Limonene       |
| 120.8                       | 0.44          | Limonene       |
| 110.6                       | 0.94          | Carvone        |
| 108.5                       | 0.54          | Limonene       |
| 43.3                        | 0.89          | Carvone        |
| 42.6                        | 0.95          | Carvone        |
| 41.2                        | 0.53          | Limonene       |
| 31.4                        | 0.91          | Carvone        |
| 30.9                        | 0.53          | Limonene       |
| 30.7                        | 0.46          | Limonene       |
| 28.1                        | 0.49          | Limonene       |
| 23.6                        | 0.51          | Limonene       |
| 21.0                        | 0.52          | Limonene       |
| 20.7                        | 1.03          | Carvone        |
| 15.8                        | 1.00          | Carvone        |

*IGD, 512 scans, D1 = 30 sec
Table SI-6. Deconvolution results for the $^{13}$C NMR spectrum* of 3,5-dimethylphenol:2,5-dimethylphenol mixture from Table 3.

| Peak chemical shift ($\delta$ ppm) | Peak Integral | Peak Assignment       |
|-----------------------------------|---------------|-----------------------|
| 155.5                             | 0.58          | 3,5-dimethylphenol    |
| 153.7                             | 1.09          | 2,5-dimethylphenol    |
| 139.7                             | 1.25          | 3,5-dimethylphenol    |
| 137.2                             | 1.05          | 2,5-dimethylphenol    |
| 130.9                             | 1.01          | 2,5-dimethylphenol    |
| 122.7                             | 0.52          | 3,5-dimethylphenol    |
| 121.6                             | 0.99          | 2,5-dimethylphenol    |
| 120.5                             | 0.98          | 2,5-dimethylphenol    |
| 115.8                             | 1.00          | 2,5-dimethylphenol    |
| 113.2                             | 1.14          | 3,5-dimethylphenol    |
| 21.4                              | 1.02          | 3,5-dimethylphenol    |
| 21.1                              | 0.90          | 2,5-dimethylphenol    |
| 15.4                              | 1.00          | 2,5-dimethylphenol    |

*IGD, 512 scans, D1 = 30 sec

Table SI-7. Deconvolution results for the $^{13}$C NMR spectrum* of 3,5-dimethylaniline:N,N-dimethylaniline mixture from Table 3.

| Peak chemical shift ($\delta$ ppm) | Peak Integral | Peak Assignment       |
|-----------------------------------|---------------|-----------------------|
| 150.8                             | 0.18          | N,N-dimethylaniline   |
| 146.5                             | 0.58          | 3,5-dimethylaniline   |
| 139.1                             | 1.29          | 3,5-dimethylaniline   |
| 129.2                             | 0.46          | N,N-dimethylaniline   |
| 120.6                             | 0.61          | 3,5-dimethylaniline   |
| 116.8                             | 0.24          | N,N-dimethylaniline   |
| 113.2                             | 1.23          | 3,5-dimethylaniline   |
| 112.8                             | 0.47          | N,N-dimethylaniline   |
| 40.7                              | 0.41          | N,N-dimethylaniline   |
| 21.4                              | 1.00          | 3,5-dimethylaniline   |

*IGD, 512 scans, D1 = 30 sec
Table SI-8. Deconvolution results for the $^{13}$C NMR spectrum* of N,N-dimethylbenzylamine:N,N-dimethylbenzamide from Table 3.

| Peak chemical shift (δ ppm) | Peak Integral | Peak Assignment               |
|-----------------------------|---------------|------------------------------|
| 171.7                       | 1.38          | N,N,N-dimethylbenzamide      |
| 139.0                       | 1.13          | N,N,N-dimethylbenzamide      |
| 136.5                       | 1.76          | N,N,N-dimethylbenzamide      |
| 129.6                       | 1.70          | N,N,N-dimethylbenzamide      |
| 129.2                       | 2.33          | N,N,N-dimethylbenzamide      |
| 128.4                       | 3.37          | N,N,N-dimethylbenzamide      |
| 128.3                       | 2.24          | N,N,N-dimethylbenzamide      |
| 127.2                       | 3.58          | N,N,N-dimethylbenzamide      |
| 1271                        | 1.15          | N,N,N-dimethylbenzamide      |
| 64.5                        | 1.10          | N,N,N-dimethylbenzamide      |
| 45.5                        | 2.00          | N,N,N-dimethylbenzamide      |
| 39.7                        | 2.23          | N,N,N-dimethylbenzamide      |
| 35.5                        | 1.89          | N,N,N-dimethylbenzamide      |

*IGD, 512 scans, D1 = 30 sec

Table SI-9. Deconvolution results for the $^{13}$C NMR spectrum* of 5,8,14,17-tetraoctyloxy-2,11-dithia[3.3]paracyclophane and 6,9,14,17-tetraoctyloxy-2,11-dithia-[3.3]paracyclophane.

| Peak chemical shift (δ ppm) | Peak Integral | Peak Assignment |
|-----------------------------|---------------|----------------|
| 150.7                       | 1.25          | $C_{\text{ar}}$ |
| 150.2                       | 0.73          | $C_{\text{ar}}$ |
| 125.4                       | 1.59          | $C_{\text{ar}}$ |
| 125.2                       | 0.92          | $C_{\text{ar}}$ |
| 114.8                       | 1.05          | $C_{\text{ar}}$ |
| 113.9                       | 1.93          | $C_{\text{ar}}$ |
| 69.1                        | 1.00          | CH$_2$          |
| 69.0                        | 1.89          | CH$_2$          |
| 26.5                        | 1.51          | CH$_2$          |
| 26.4                        | 2.20          | CH$_2$          |
| 22.8                        | 1.36          | CH$_2$          |
| 22.8                        | 2.50          | CH$_2$          |
| 14.3                        | 1.50          | CH$_3$          |
| 14.3                        | 2.55          | CH$_3$          |

*BBD, 512 scans, D1 = 30 sec.
Table SI-10. Deconvolution results for the $^{13}$C NMR spectrum* of allyl lactide from Table 4.

| Peak chemical shift (δ ppm) | Peak Integral | Peak Assignment |
|-----------------------------|---------------|-----------------|
| 167.2                       | 0.49          | C=O             |
| 166.4                       | 0.60          | C=O             |
| 166.1                       | 0.12          | C=O             |
| 165.3                       | 0.31          | C=O             |
| 130.7                       | 1.54          | C(alkene)       |
| 130.0                       | 0.76          | C(alkene)       |
| 121.6                       | 0.76          | C(alkene)       |
| 120.4                       | 1.80          | C(alkene)       |
| 76.3                        | 1.01          | CH              |
| 75.5                        | 1.83          | CH              |
| 73.0                        | 0.86          | CH              |
| 72.5                        | 1.81          | CH              |
| 36.5                        | 0.98          | CH$_2$          |
| 34.4                        | 1.85          | CH$_2$          |
| 18.0                        | 1.00          | CH$_3$          |
| 16.1                        | 1.96          | CH$_3$          |

*BBD, 512 scans, D1 = 2 sec.

Table SI-11. Deconvolution results for the $^{13}$C NMR spectrum* of the peptoid model from Table 4.

| Peak chemical shift (δ ppm) | Peak Integral | Peak Assignment |
|-----------------------------|---------------|-----------------|
| 171.0                       | 0.35          | Unassigned      |
| 170.7                       | 0.47          | Unassigned      |
| 137.4                       | 0.60          | Rotomer A       |
| 136.6                       | 0.49          | Rotomer B       |
| 129.0                       | 1.81          | Unassigned      |
| 128.6                       | 2.31          | Unassigned      |
| 128.0                       | 2.24          | Unassigned      |
| 127.7                       | 0.93          | Unassigned      |
| 127.3                       | 1.17          | Unassigned      |
| 126.3                       | 1.74          | Unassigned      |
| 54.3                        | 0.90          | Rotomer B       |
| 50.6                        | 1.12          | Rotomer A       |
| 35.5                        | 0.75          | Rotomer A       |
| 33.7                        | 0.68          | Rotomer B       |
| 21.9                        | 1.00          | Rotomer A       |
| 21.5                        | 0.75          | Rotomer B       |

*BBD, 512 scans, D1 = 2 sec.
Table SI-12. Deconvolution results for the $^{13}$C NMR spectrum* of N-acyl-D-glucosamine from Table 4.

| Peak chemical shift (δ ppm) | Peak Integral | Peak Assignment |
|-----------------------------|---------------|-----------------|
| 170.1                       | 0.06          | Minor Anomer    |
| 169.8                       | 0.80          | Major Anomer    |
| 96.0                        | 0.10          | Minor Anomer    |
| 91.1                        | 1.05          | Major Anomer    |
| 77.2                        | 0.07          | Minor Anomer    |
| 74.8                        | 0.11          | Minor Anomer    |
| 72.5                        | 1.08          | Major Anomer    |
| 71.7                        | 1.09          | Major Anomer    |
| 71.3                        | 0.07          | Minor Anomer    |
| 71.0                        | 1.10          | Major Anomer    |
| 61.6                        | 1.10          | Major Anomer    |
| 57.7                        | N/A           | Minor Anomer    |
| 54.8                        | 1.08          | Major Anomer    |
| 31.2                        | 0.06          | Minor Anomer    |
| 23.5                        | 0.10          | Minor Anomer    |
| 23.2                        | 1.00          | Major Anomer    |

*BBD, 512 scans, D1 = 2 sec

Table SI-13. Deconvolution results for the $^{13}$C NMR spectrum* of the 3,5-dimethylphenol:2,5-dimethylphenol mixture (with addition of O$_2$) from Table 5.

| Peak chemical shift (δ ppm) | Peak Integral | Peak Assignment |
|-----------------------------|---------------|-----------------|
| 155.5                       | 0.86          | 3,5-dimethylphenol |
| 153.6                       | 0.34          | 2,5-dimethylphenol |
| 139.7                       | 1.72          | 3,5-dimethylphenol |
| 137.2                       | 0.43          | 2,5-dimethylphenol |
| 130.9                       | 0.69          | 2,5-dimethylphenol |
| 122.7                       | 1.69          | 3,5-dimethylphenol |
| 121.6                       | 0.71          | 2,5-dimethylphenol |
| 120.5                       | 0.42          | 2,5-dimethylphenol |
| 115.8                       | 0.73          | 2,5-dimethylphenol |
| 113.1                       | 3.71          | 3,5-dimethylphenol |
| 21.4                        | 2.00          | 3,5-dimethylphenol |
| 21.1                        | 0.43          | 2,5-dimethylphenol |
| 15.4                        | 0.55          | 2,5-dimethylphenol |

*BBD, 64 scans, D1 = 2 sec
Table SI-14. Deconvolution results for the $^{13}$C NMR spectrum of Poly(lactic acid) (P(LA)) from Table 6.

| Peak chemical shift (δ ppm) | Peak Integral | Peak Assignment     |
|---------------------------|--------------|--------------------|
| 20.7                      | 1.09         | CH$_3$ backbone    |
| 16.9                      | 1.11         | CH$_3$ backbone    |
| 16.9-16.8                 | 25.01        | CH$_3$ backbone    |
| 14.18                     | 1.00         | CH$_3$ end-group   |

*For backbone integration, the four signals were added. These data suggest DP = 27.1.

Table SI-15. Deconvolution results for the $^{13}$C NMR spectrum* of poly(4-methyl-oxazoline) P(Ox) from Table 6.

| Peak chemical shift (δ ppm) | Peak Integral | Peak Assignment     |
|---------------------------|--------------|--------------------|
| 37.4                      | 0.70         | CH$_3$ backbone    |
| 37.1                      | 0.30         | CH$_3$ backbone    |
| 21.8                      | 9.68         | CH$_3$ end-group   |
| 21.2                      |              | CH$_3$ end-group   |
| 20.1                      |              | CH$_3$ end-group   |

*BBD, 512 scans, D1 = 30 sec. For backbone integration, the three signals were added. These data suggest DP = 9.7.

Table SI-16. Deconvolution results for the $^{13}$C NMR spectrum* of poly(4-methyl-oxazoline) P(Ox) from Table 6.

| Peak chemical shift (δ ppm) | Peak Integral | Peak Assignment     |
|---------------------------|--------------|--------------------|
| 37.5                      | 0.80         | CH$_3$ backbone    |
| 37.1                      | 0.20         | CH$_3$ backbone    |
| 21.8                      | 17.68        | CH$_3$ end-group   |
| 21.3                      |              | CH$_3$ end-group   |
| 20.7                      |              | CH$_3$ end-group   |

*BBD, 512 scans, D1 = 30 sec. For backbone integration, the three signals were added. These data suggest DP = 17.7.

Table SI-17. Deconvolution results for the $^{13}$C NMR spectrum of Poly(norbornene octanoate) P(NO) from Table 6.

| Peak chemical shift (δ ppm) | Peak Integral | Peak Assignment     |
|---------------------------|--------------|--------------------|
| 142.0                     | 0.35         | CH backbone        |
| 140.6                     | 0.87         | CH backbone        |
| 137.6-137.5               | 0.67         | CH backbone        |
| 133.9-132.1               | 35.23        | CH backbone        |
| 114.5-113.3               | 2            | CH$_2$ end-group   |

*For backbone integration, the four signals were added and then divided by two, because there are 2 backbone carbons to account for. These data suggest DP = 18.6.
GC, HPLC, MALDI, IR, HRMS Data:

Figure S-1: GC Data of camphor:fenchone (mol % fenchone = 39.2%) from Figure 1.
**Area % Report**

Data File: C:\Documents and Settings\User\Desktop\Data\DALO\DALO20131205-007-BE10.dat  
Method: C:\Documents and Settings\User\Desktop\DALO\_Dorothee-30min---0.1%---Fast.met  
Acquired: 12/5/2013 5:53:01 PM  
Printed: 12/18/2013 5:32:39 PM

### UV Detector  
**Ch1-254nm**  
**Results**

| Retention Time | Area  | Area % | Height | Height % |
|----------------|-------|--------|--------|----------|
| 1.702          | 72671 | 57.58  | 11792  | 62.84    |
| 2.412          | 53536 | 42.42  | 6972   | 37.16    |
| **Totals**     | **126207** | **100.00** | **18764** | **100.00** |

Figure S-2: HPLC of 5,8,14,17-tetraoctyloxy-2,11-dithia[3.3]paracyclophane and 6,9,14,17-tetraoctyloxy-2,11-dithia-[3.3]paracyclophane
Figure S-3: MALDI-ToF spectrum of poly(norbornene octanoate) (P(NO))
Figure S-4: MALDI-ToF spectrum of poly(lactic acid) 1 (PLA1)
Figure S-5: MALDI-ToF spectrum of poly(lactic acid) 2 (PLA2)
Figure S-6: MALDI-ToF spectrum of poly(2-methyloxazoline) 1 (P(Ox)1)
Figure S-7: MALDI-ToF spectrum of poly(2-methyloxazoline) 2 (P(Ox)2)
Figure S-8: IR spectrum of 3.
Figure S-9: HRMS of 3.