Supporting information

Ring-opening metathesis polymerization of a naturally derived macrocyclic glycolipid

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Table-1S. The effect of catalyst loading on the ROMP of LSL.

<table>
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<th>Initiator</th>
<th>Initiator (mol % relative to monomer)</th>
<th>Monomer conversion (%)</th>
<th>$M_n$ (x 10^3)</th>
<th>$M_w/M_n$</th>
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Figure 2S. G2 catalyzed ROMP of LSL at 33 °C: influence of the reaction media on monomer conversion vs. reaction time.
Figure-3S. G2 catalyzed ROMP of LSL at 33 °C: influence of the reaction media on pLSL $M_n$ vs. reaction time.
**Experimental Methods: NMR.** All 2D NMR experiments were performed on a Bruker AVIII 500 with Z axis gradients.

**HSQC.** The edited HSQC used a standard Bruker pulse program (hsqcedetgpsisp or hsqcedetgpssp.3), which included adiabatic inversion pulses on $^{13}$C. Hsqcedetgpssp.3 provided spectra with superior phase behavior. Typical spectral widths were 2500 Hz and 20000 Hz for proton and carbon, respectively, with 2K and 512 points in the respective proton and carbon dimensions. Four scans were taken for each t1 increment.

**HSQC-TOCSY.** The HSQC-TOCSY used the standard Bruker pulse program hsqcdietgps. TOCSY mixing times were 80 ms. Typical spectral widths were 2500 Hz and 20000 Hz for proton and carbon, respectively, with 2K and 512 points in the respective proton and carbon dimensions. Twenty four scans were acquired for each t1 increment.

**COSY.** Magnitude mode COSY spectra used standard Bruker pulse program cosygpppqf. Typical spectral widths were 5000 Hz in both dimensions while 1K and 256 points were taken in the F2 and F1 dimensions, respectively. Typically, 1 scan per t1 increment was acquired.

**HMBC.** The HMBC used standard Bruker pulse program hmbcgpl2ndqf. Typical spectra widths were 5000 Hz and 28000 Hz for proton and carbon, respectively, with 1600 and 1024 points in the F2 and F1 dimensions, respectively. Typically, 24 scans per t1 increment were acquired.

**Discussion of NMR assignments.** Assignment of lactonic sophorolipid (LSL) monomer carbon and proton NMR spectra was accomplished with the help of two-dimensional COSY, HSQC, HMBC, and HSQC-TOCSY spectra. In Figure-9S, COSY correlates protons that are coupled over 2 or 3 bonds. In Figure-6S, HSQC spectra correlate the chemical shifts of carbons with the chemical shifts of directly attached protons. The phase of the HSQC peak, expressed as the color in the plot, indicates the multiplicity. In an HSQC-TOCSY spectrum as in Figure-7S-1 and Figure-7S-2, the proton signal from an
HSQC carbon-proton pair is then transferred further to protons that are coupled. The result is that signals appear at the proton shift of the neighbors but retain the original carbon shift. The length of the TOCSY mixing time determines the number of transfer steps and was chosen to be 80 ms. Each of the carbon-bound protons from a single sugar ring forms a discrete proton spin system, and for an 80 ms mixing time, the signal is transferred among all protons within the ring. Since proton-proton coupling does not occur across the ester link, there is no transfer to beyond the ring. Use of HSQC and HSQC-TOCSY together with COSY greatly simplifies the task of assignment and allows all the protons on a given ring to be assigned.

In Figure-8S, HMBC cross peaks connect protons with carbons that are 2, 3, or sometimes 4 bonds apart and can provide additional information not present in the HSQC-TOCSY such as connections across glycosidic bonds. For example, C17 (77.68 ppm) can be easily identified in Figure-7S-1, as it shows a HSQC-TOCSY cross peak with the H18 methyl group. In addition, in Figure-8S, C17 (77.68 ppm) shows a HMBC cross peak to H1′ (101.77 ppm), and symmetrically, C1′ shows a HMBC cross peak to H17. Since H17 also shows a connection to the H18 methyl, these HMBC cross peaks establish unambiguous identification of the ring spin systems. Assignment can proceed from either end of the ring. The following is an example: from the HMBC connection above, the H1′ assignment can be made. Then, as shown in Figure-9S, the COSY cross peak between H1′ and H2′ allows assignment of H2′ to 3.217 ppm. The assignment of H3′ is not possible from only COSY due to proton overlap between H3′, H3″, and H5′,
but requires the HSQC-TOCSY. Since the carbon shifts $C_{3}', C_{3}'', C_{5}'$ are distinct, these protons are resolved into the carbon dimension of the HSQC-TOCSY. In Figure-7S-2, at $C_{3}'$, there are proton-proton connectivity’s from $H_{3}'$ to $H_{1}'$ (4.341 ppm), $H_{2}'$ (3.217 ppm), and $H_{4}'$ (3.084 ppm). At $C_{2}'$, there are proton-proton connectivity’s from $H_{2}'$ to $H_{1}'$ (4.341 ppm), $H_{3}'$ (3.373 ppm), and $H_{4}'$ (3.084 ppm). Inspection of the intensities indicates the $H_{3}'$ assignment to be 3.373 ppm since, despite the oscillating character of intensity transfer during TOCSY mixing, experience indicates the single-step transfer is usually stronger than longer range transfers. These proton-proton connectivity’s at different carbon shifts provide a self-consistency check. This procedure is repeated until all carbon-proton pairs are assigned, and they are labeled in Figure-4S and 5S.

**Figure-4S.** $^1$H NMR of LSL (500 MHz, DMSO- $d_6$).
Figure-5S. $^{13}$C NMR (inverse-gated decoupling) of LSL (300 MHz, DMSO- $d_6$).
Figure-6S. HSQC spectrum of LSL (500 MHz, DMSO-d$_6$).
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Figure-9S. COSY spectrum of LSL (500 MHz, DMSO-d$_6$).
Figure 10S. $^1$H NMR (500 MHz, DMSO-d$_6$ with 5% D$_2$O) of pLSL synthesized by: a) G2 and b) G3. In both 10S-a and 10S-b, 75% of the carbon-carbon double bonds are trans.