Supporting Information

General

^{1}H NMR spectra were recorded with a JEOL JNMGSX-400 spectrometer. XRD patterns were measured with Rigaku RINT InPlane/ultraX18SAXS-IR using CuK_α radiation. The voltage was set to 40 kV, and the current was set to 200 mA. IR spectra were measured on a Horiba FT-710 spectrometer.

Chemical shifts of 1-PTHF precipitate

^{1}H-NMR (DMSO-d_6) δ 1.48-1.51 (m, 14H), 2.91 (t, 1H, J = 8.43 Hz), 2.99-3.06 (m, 4H), 3.12 (dd, 1H, J = 8.06, 3.3Hz), 3.18-3.79 (m, 97H), 4.03-4.08 (m, 1H), 4.59 (d, 1H, J = 7.7 Hz), 4.97 (m, 4H), 5.40 (d, 1H, J = 3.3 Hz).

Chemical shifts and ^{1}H NMR spectrum of 2-PTHF precipitate

^{1}H-NMR (DMSO-d_6) δ 1.48-1.51 (m, 6H), 3.00 (dd, 6H, J = 9.9, 3.3 Hz), 3.23 (s, 18H), 3.32-3.53 (m, 60H), 3.69-3.77 (m, 12H), 4.96 (d, 6H, J = 3.3 Hz).

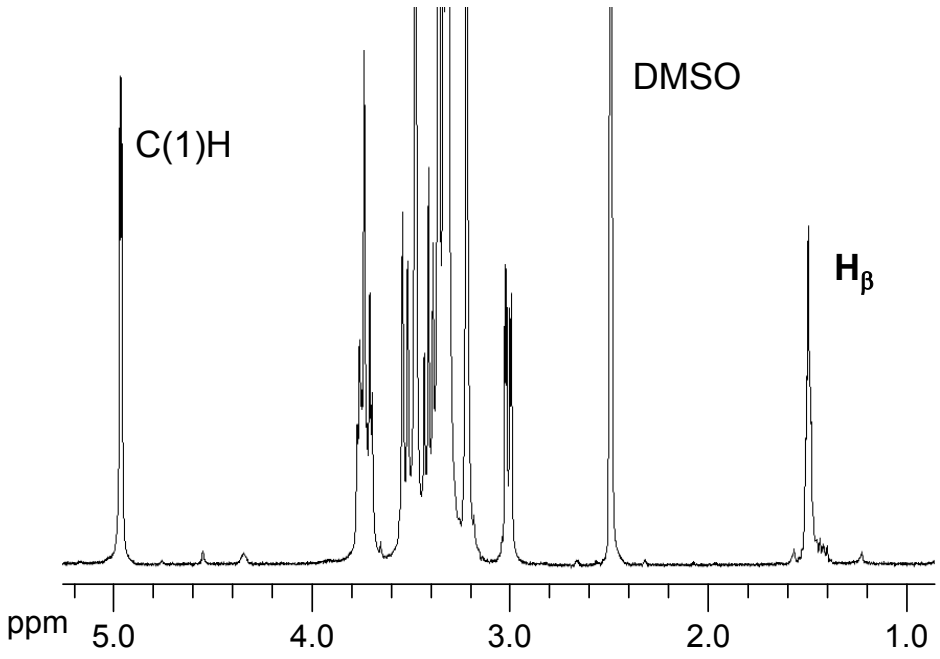

Figure S1. ^{1}H NMR spectrum of the **2**-PTHF precipitate in DMSO-d_6 at 25 ºC.

XRD patterns, Chemical shifts, and ^{1}H NMR spectrum of 1-PCL precipitate

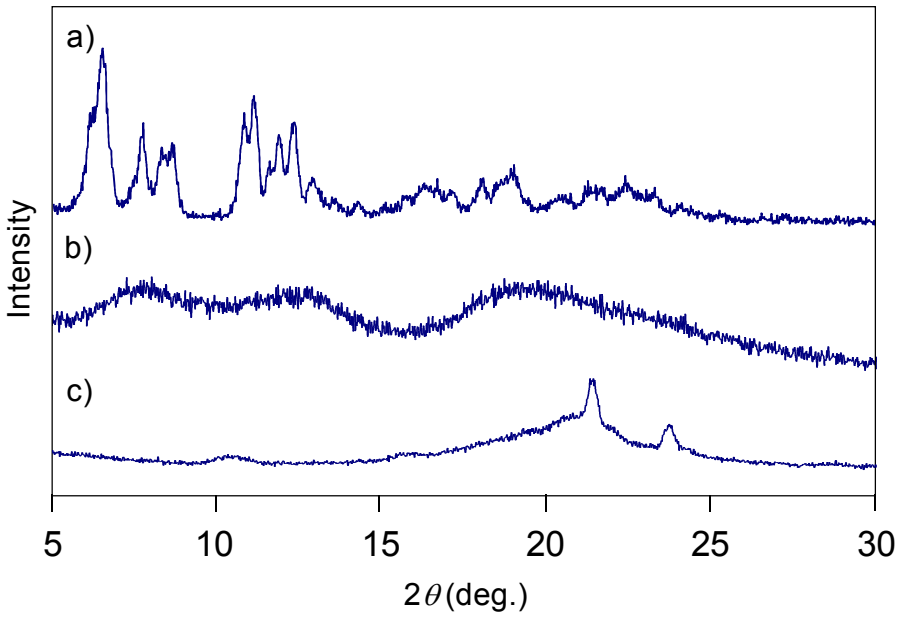

Figure S2. XRD patterns of a) **1**-PCL precipitate, b) **1**, and c) PCL.

^{1}H-NMR (DMSO-d_6) δ 1.22-1.32 (m, 9H), 1.48-1.58 (m, 18H), 2.23-2.28 (m 9H), 2.91 (t, J = 8.43 Hz, 1H), 2.99-3.06 (m, 4H), 3.12 (dd, 1H, J = 8.06, 3.3Hz), 3.18-3.79 (m, 83H) ,3.97 (t, 9H, J = 6.6 Hz), 4.03-4.08 (m, 1H), 4.59 (d, 1H, J = 7.7 Hz), 4.97 (m, 4H), 5.40 (d, 1H, J = 3.3 Hz).

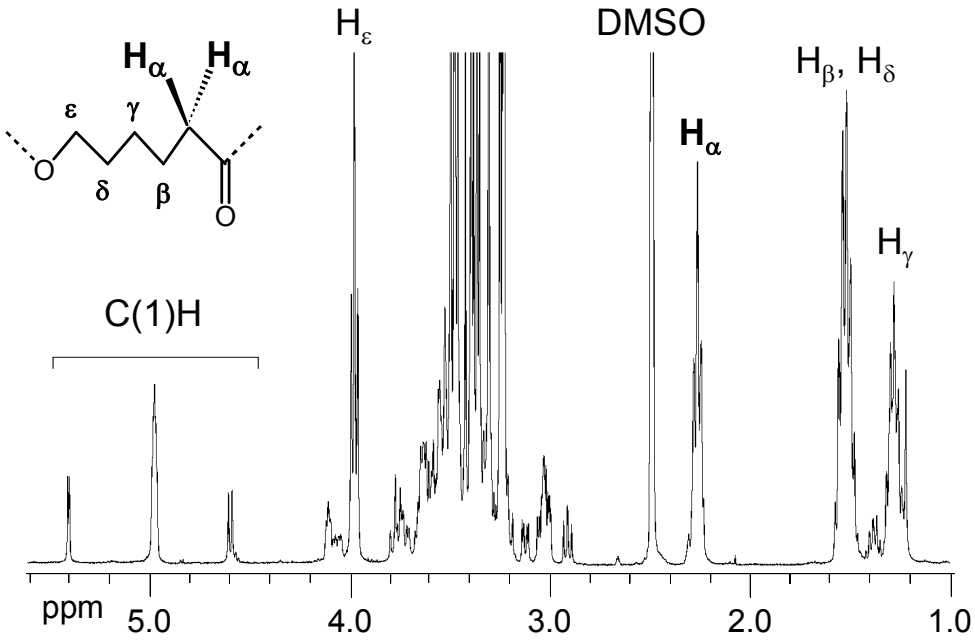

Figure S3. ^{1}H NMR spectrum of the **1**-PCL precipitate in DMSO-d_6 at 25 ºC.

XRD patterns, Chemical shifts and ^{1}H NMR spectrum of 2-PCL precipitate

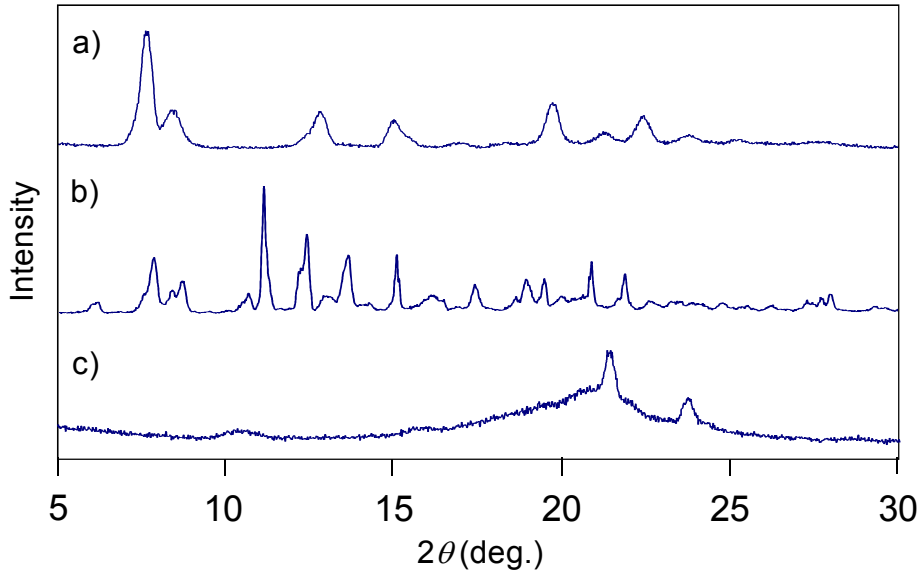

Figure S4. XRD patterns of a) **2**-PCL precipitate, b) **2**, and c) PCL.

^{1}H-NMR (DMSO-d_6) δ 1.22-1.32 (m, 2H), 1.48-1.58 (m, 4H), 2.32-2.3 (m, 2H), 3.00 (dd, 6H, J = 9.9, 3.3 Hz), 3.22 (s, 18H), 3.31-3.53 (m, 54H), 3.69-3.77 (m, 12H), 3.97 (t, 2H, J = 6.6 Hz), 4.96 (d, 6H, J = 3.3 Hz).

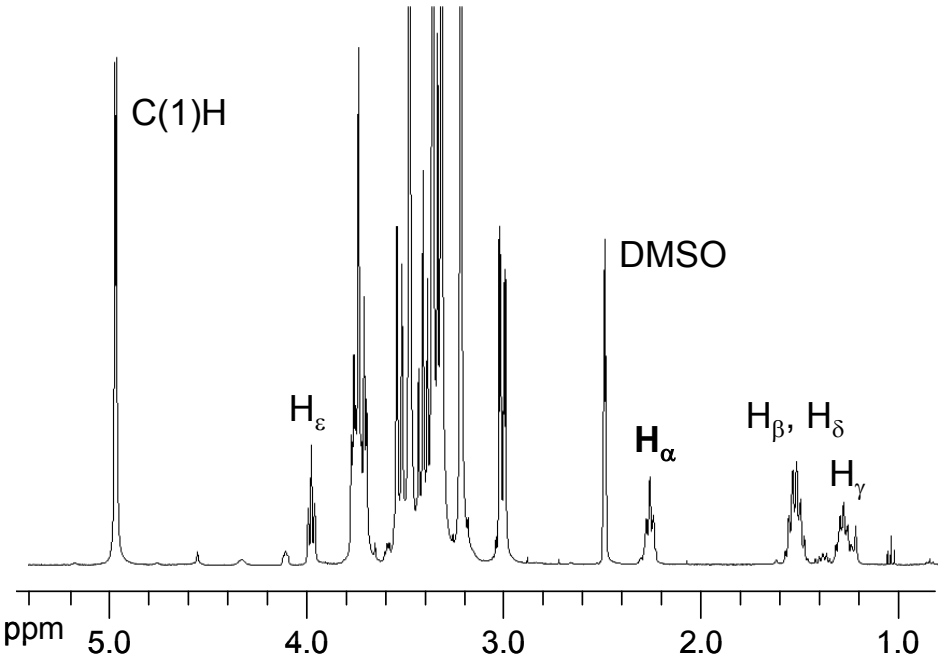

Figure S5. ^{1}H NMR spectrum of the **2**-PCL in DMSO-d_6 at 25 ºC.

Chemical shifts of 1-PAA precipitate

^{1}H-NMR (DMSO-d_6) δ 1.16-1.66 (m, 10H), 2.20 (m, 5H), 2.91 (t, J = 8.43 Hz, 1H), 2.99-3.06 (m, 4H), 3.12 (dd, 1H, J = 8.06, 3.3Hz), 3.18-3.79 (m, 83H) , 4.03-4.08 (m, 1H), 4.59 (d, 1H, J = 7.7 Hz), 4.97 (m, 4H), 5.40 (d, 1H, J = 3.3 Hz), 12.25 (m, 10H).

XRD patterns, Chemical shifts, and ^{1}H NMR spectrum of 1-PPG precipitate

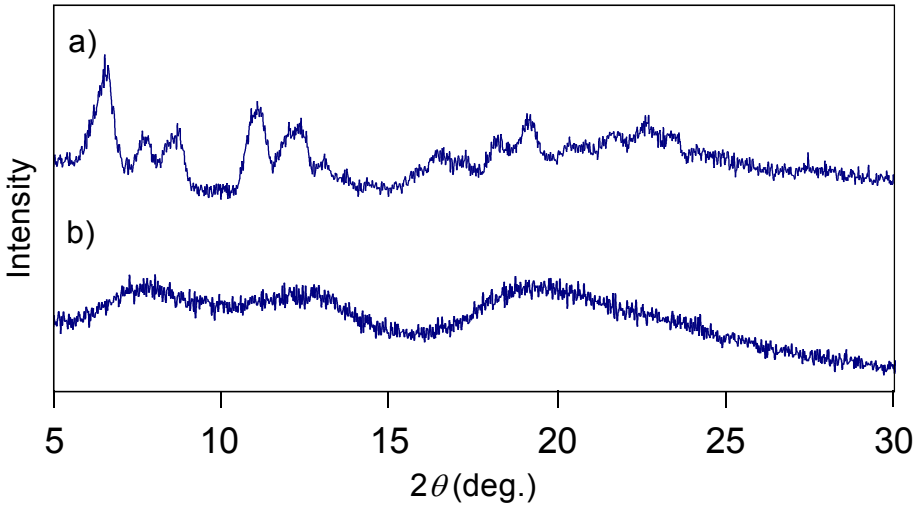

Figure S6. XRD patterns of a) **1**-PPG precipitate and b) **1**.

^{1}H-NMR (DMSO-d_6) δ 1.03 (d, 6H, J = 6.2 Hz), 2.91 (t, J = 8.43 Hz, 1H), 2.99-3.06 (m, 4H), 3.12 (dd, 1H, J = 8.06, 3.3Hz), 3.18-3.79 (m, 89H) , 4.03-4.08 (m, 1H), 4.59 (d, 1H, J = 7.7 Hz), 4.97 (m, 4H), 5.40 (d, 1H, J = 3.3 Hz).

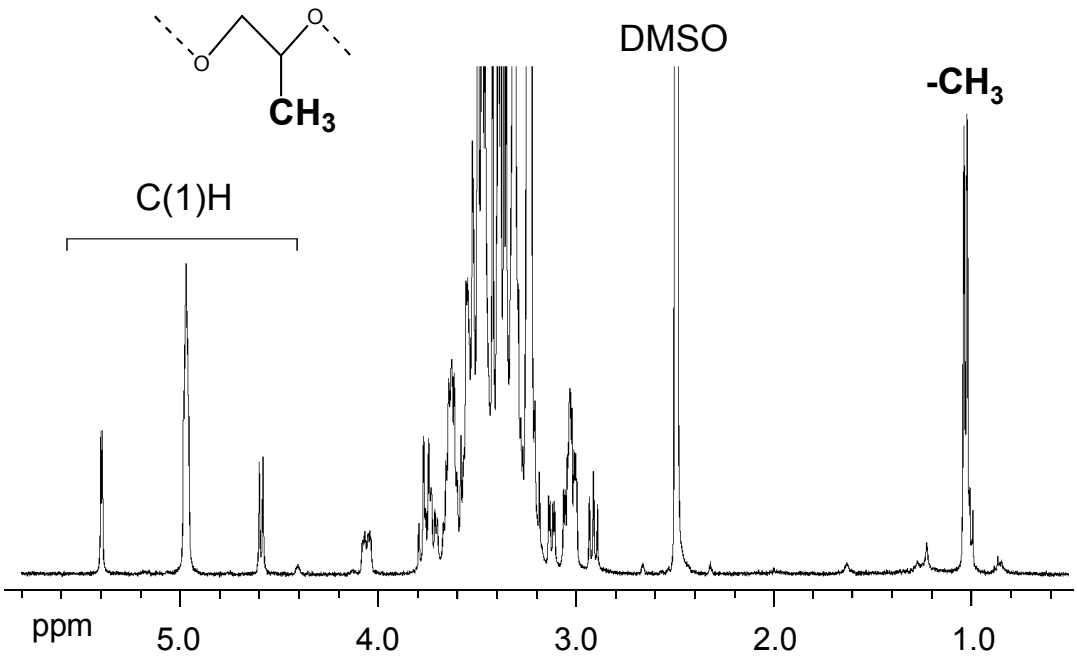

Figure S7. ^{1}H NMR spectrum of the **1**-PPG precipitate in DMSO-d_6 at 25 ºC.

XRD patterns, Chemical shifts, and ^{1}H NMR spectrum of 2-PPG precipitate

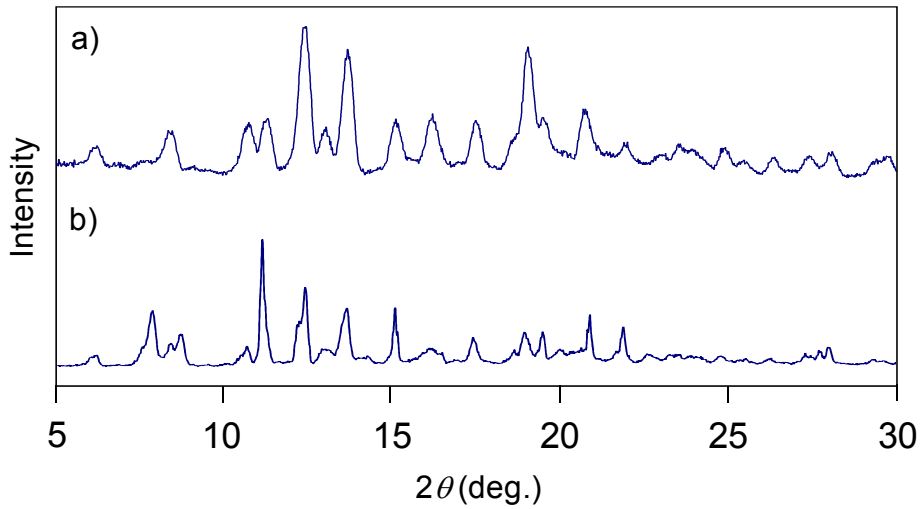

Figure S8. XRD patterns of a) **2**-PPG precipitate and b) **2**.

^{1}H-NMR (DMSO-d_6) δ 1.02 (d, 17H, J = 7.0 Hz), 3.00 (dd, 6H, J = 9.6, 3.1 Hz), 3.21 (s, 18H), 3.30-3.54 (m, 71H), 3.68-3.78 (m 12H), 4.96 (d, 6H, J = 3.3 Hz).

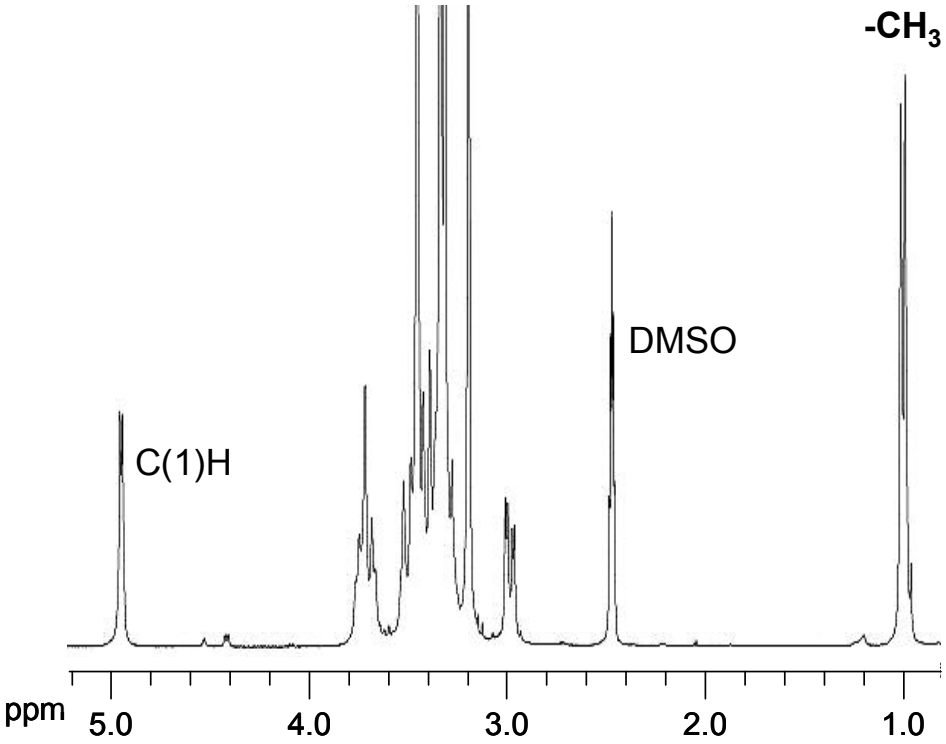

Figure S9. ^{1}H NMR spectrum of the **2**-PPG precipitate in DMSO-d_6 at 25 ºC.