Electronic Supplementary Information for

Cu(triNHC)-Catalyzed Polymerization of Glycidol to Produce Ultralow-Branched Polyglycerol

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I. Experimental procedures

Materials. Glycidol (96.0%), $Cu(OTf)_2$ (98.0%), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (98%), copper iodide (99.999%) were obtained from Sigma Aldrich. 1,3-Bis(2,6-diisopropylphenyl)imidazole-2-ylidene (98.0%) was obtained from Tokyo Chemical Industry. Toluene (99.9%) was sourced from Samchun Chemicals. Glycidol and toluene were dried with CaH_2 and distilled prior to use. Catalysts A and B were prepared as described in the previous literature.[1]

Measurements. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Jeol Resonance ECZ600R (600 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of a peak at 2.50 ppm for DMSO-d_6. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Jeol Resonance ECZ600R (150 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of a peak at 39.52 ppm for DMSO-d_6. ^{1}H diffusion-ordered spectroscopy (DOSY) was recorded on a Bruker AVANCE III HD 300 spectrometer at 25 °C. All samples were dissolved in DMSO-d_6. Matrix-assisted laser desorption/ionization time-of-flight(MALDI-ToF) measurement was performed using autoflex maX from Bruker. 2,5-Dihydroxybenzoic acid(DHB) was used as the matrix. For DMF-SEC, three polystyrene-gel columns [KD-802 (from Shodex); pore size, 150 Å; 8 mm i.d. × 300 mm, KD-803 (from Shodex); pore size, 500 Å; 8 mm i.d. × 300 mm, KD-804 (from Shodex); pore size, 1500 Å; 8 mm i.d. × 300 mm] were connected to a PU-4180 pump, an RI-4030 refractive-index detector, and a UV-4075 ultraviolet detector (JASCO); the flow rate was maintained at 1.0 mL min^{-1} . The columns were calibrated against 13 standard poly(ethylene glycol) (PEO) samples (Agilent Technologies; Mp = 980–811 500; M_w/M_n = 1.03–1.11) to analyze the obtained polymer samples. Differential scanning calorimetry (DSC) was conducted on polymer samples under a dry nitrogen flow (40 ml/min) in the temperature range of -70~+70 ^{o}C at a heating or cooling rate of 10 °C/min on a Q2000 calorimeter (TA Instruments).

General procedure for polymerization of glycidol

Glycidol (148.2 mg, 2 mmol), catalysts (21.2 mg, 2 mol%), and toluene (1.0 ml) were added to the reaction vial. The mixture was stirred at the indicated temperature for 16 h under the nitrogen atmosphere. Then, the reaction mixture was washed with diethyl ether to remove the unreacted monomer. The product was dried at 50 ^{o}C for 1 day before obtaining the yield and sample analysis.

Procedure for catalyst recycling experiment

Glycidol (148.2 mg, 2 mmol), catalyst (21.2 mg, 2 mol%), and toluene (1.0 ml) were added to the reaction vial. The mixture was stirred at the indicated temperature for 16 h under the nitrogen atmosphere. After the reaction, glycidol (148.2 mg, 2 mmol) was added repeatedly in each cycle. Then, the reaction mixture was washed with diethyl ether to remove the unreacted monomer. The product was dried at 50 ^{o}C for 1 day before obtaining the yield and sample analysis.

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[1] Seo. C.; Cheong. Y.-J.; Yoon. W.; Kim. J.; Shin. J.; Yun. H.; Kim. S.-J.; Jang. H.-Y.; Mononuclear Copper Complexes with Tridentate Tris(*N*-heterocyclic carbene): Synthesis and Catalysis of Alkyne-Azide Cycloaddition. Organometallics **2021**, *40*, 16-22

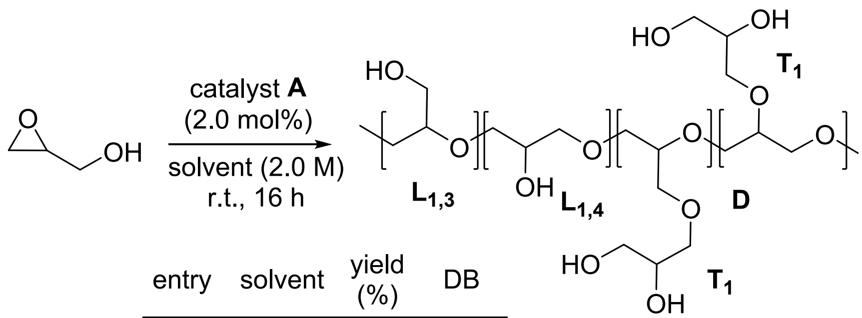
II. Additional Polymerization Data

Table S1. Previously reported DB values without using unprotected glycidol

catalyst	initiator	temp (°C)	time	DB	ref
$Sn(OTf)_2$	isoamyl alcohol	20	2.5h	0.21	8
$Sn(OTf)_2$	isoamyl alcohol	0	42h	0.20	8
$Sn(OTf)_2$	isoamyl alcohol	-20	96h	0.15	8
PBS	--	80	72h	0.25	27
DMC-DEM	--	110	5h	0.27	25

PBS: phosphate buffered saline with pH = 6.0
DMC: double metal cyanide, DEM: diethyl malonate

Table S2. Solvent screening of glycidol polymerization



entry	solvent	yield (%)	DB
1	toluene	94	0.18
2	dioxane	--	--
3	CH_3CN	3.5	--

Table S3. Detailed unit distribution of polymers of Table 1

Region	Chemical shift (ppm)	Entry 1	Entry 2	Entry 3	Entry 4	Entry 5	Entry 8	Entry 9
T_2	82.5-83.0	0.032	0	0	0.25	0.16	0	0
$L_{1,3}$	79.7-80.4	1.00	1.00	1.00	1.00	1.00	1.00	1.00
D	77.7-78.3	0.29	0.085	0.14	1.05	1.57	1.62	1.11
$2L_{1,4}$	72.6-73.1	3.21	1.92	2.26	18.88	12.6	7.22	6.69
2D, $2T_1$	70.4-72.0	2.98	1.70	2.21	15.27	12.83	9.35	8.61
$L_{1,3}$, $L_{1,4}$	68.5-69.7	2.00	1.66	1.74	8.27	7.01	4.05	3.30
T_1	62.9-63.3	0.71	0.22	0.42	8.85	4.61	2.87	3.46
$2T_2$	61.2-61.8	0.055	0	0.00	1.11	0.89	0.17	0.14
$L_{1,3}$	60.7-61.2	0.97	1.00	0.92	1.5	0.92	1.09	0.90
Terminal (%)		20.4	9.7	15.6	44.2	35.0	32.2	39.3
T_1 (%)		19.5	9.7	15.6	43.0	33.8	31.2	38.5
T_2 (%)		0.9	0	0	1.2	1.2	0.9	0.8
Dendritic (%)		8.0	3.8	5.2	5.1	11.5	17.6	12.4
Linear (%)		71.6	86.5	79.2	50.7	53.5	50.2	48.4
$L_{1,3}$ (%)		27.5	44.1	37.2	4.9	7.3	10.9	11.1
$L_{1,4}$ (%)		44.1	42.4	42.0	45.8	46.2	39.3	37.2
Degree of branching[b]		0.18	0.08	0.12	0.17	0.30	0.41	0.34

[a] Obtained from inverse gated ^{13}C NMR.

[b] Degree of branching = $\frac{2D}{2D + L}$

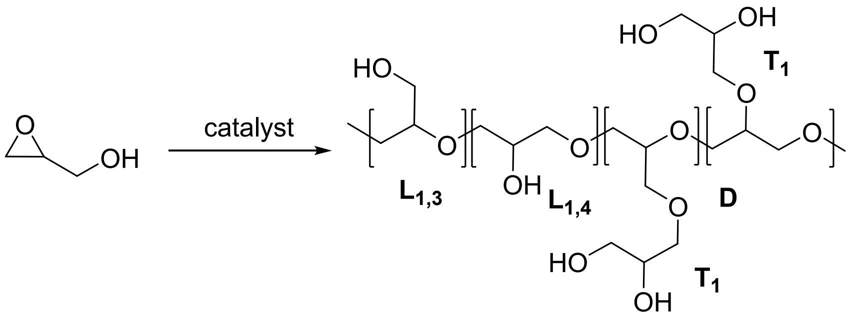
Table S4. Unit distribution of polymers obtained from recycling experiments

Region	Chemical shift (ppm)	Cycle 1	Cycle 2	Cycle 3
T_2	82.5-83.0	0.032	0	0.007
$L_{1,3}$	79.7-80.4	1.00	1.00	1.00
D	77.7-78.3	0.29	0.19	0.2
$2L_{1,4}$	72.6-73.1	3.21	2.04	1.99
2D, $2T_1$	70.4-72.0	2.98	1.96	2.00
$L_{1,3}$, $L_{1,4}$	68.5-69.7	2.00	1.77	1.74
T_1	62.9-63.3	0.71	0.25	0.42
$2T_2$	61.2-61.8	0.055	0	0.00
$L_{1,3}$	60.7-61.2	0.97	1.02	0.92
Terminal (%)		20.4	10.2	13.0
	T_1 (%)	19.5	10.2	12.7
	T_2 (%)	0.9	0	0.3
Dendritic (%)		8.0	7.7	7.9
Linear (%)		71.6	82.1	79.1
	$L_{1,3}$ (%)	27.5	40.6	39.7
	$L_{1,4}$ (%)	44.1	41.5	39.5
Degree of branching[b]		0.18	0.16	0.17

[a] Obtained from inverse gated ^{13}C NMR.

[b] Degree of branching = $\frac{2D}{2D + L}$

Table S5. Additional experimental results



entry	catalyst	temp. (°C)	time (h)	yield (%)	DB	D	$L_{1,3}/L_{1,4}$	T_1
1	**A** (1 mol%)	25	16	65	0.13	6.2	39/41	15
2	**A** (4 mol%)	25	16	95	0.25	11.2	16/50	23
3	**B** (2 mol%)	0	48	90	0.14	6.7	42/41	10
4	CuI (2 mol%)/IPr (6 mol%)	25	16	33	0.10	2.6	4.5/42	51

III. MALDI-ToF spectra

Azide addition: Ring-opening of glycidol monomer by sodium azide was conducted prior to the polymer examination. After the reaction, it was confirmed by ^{1}H NMR that all monomers were ring-opened. Accordingly, topology examination of polymers was attempted using sodium azide. The reaction was conducted with polymers, sodium azide (5 equivalents to OH), and 2.5 M of deionized water at 25 ^{o}C for 16 hours under a nitrogen atmosphere.

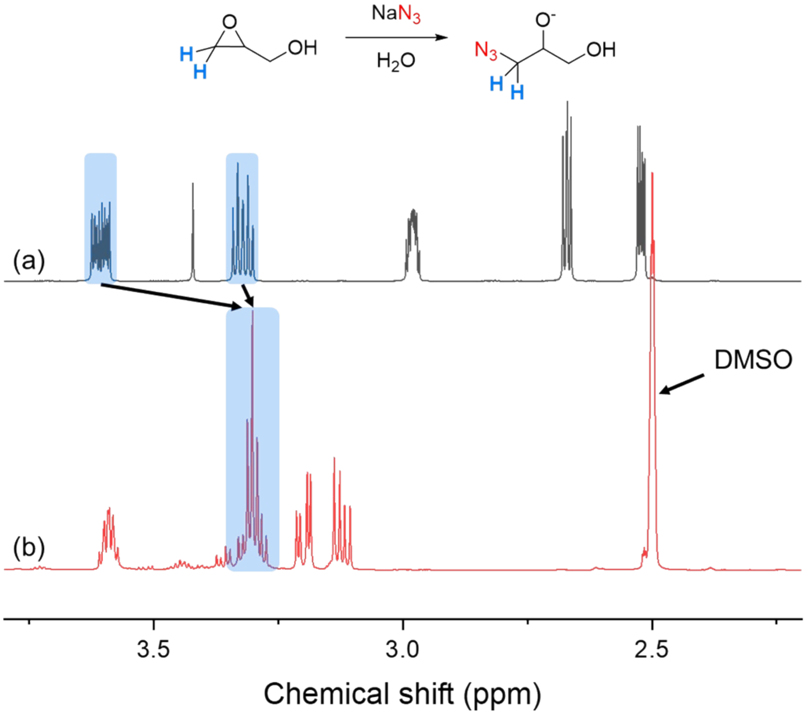
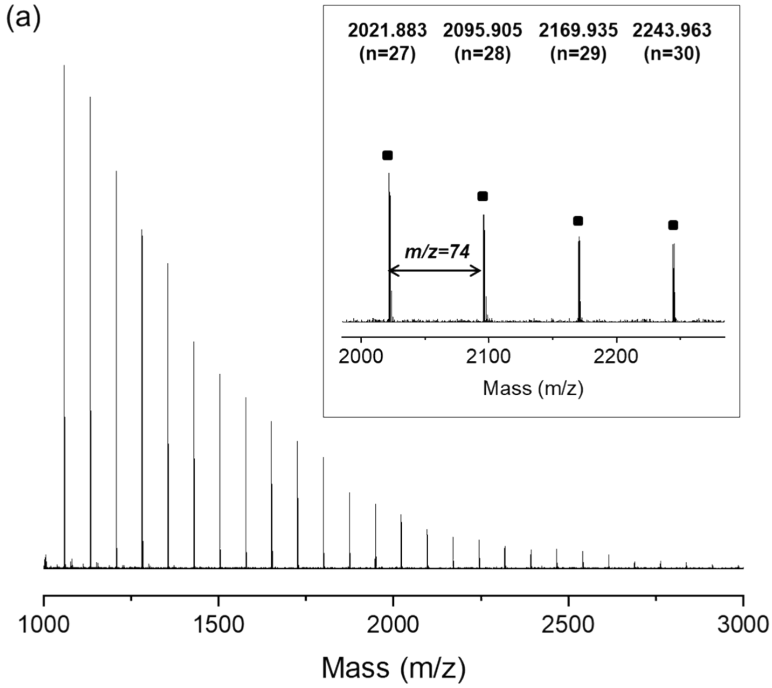


Figure S1. Ring-opening of glycidol by azide addition (a) glycidol, (b) ring-opened glycidol.



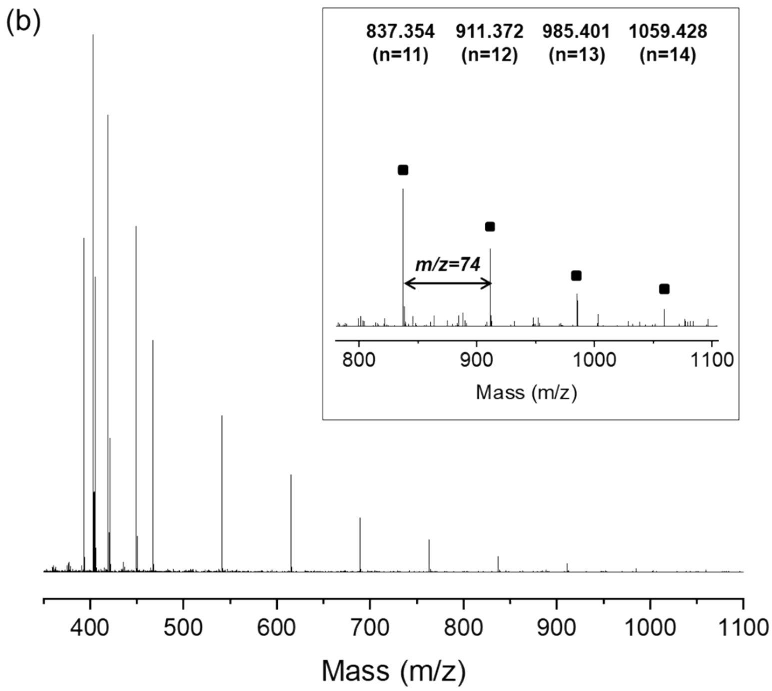
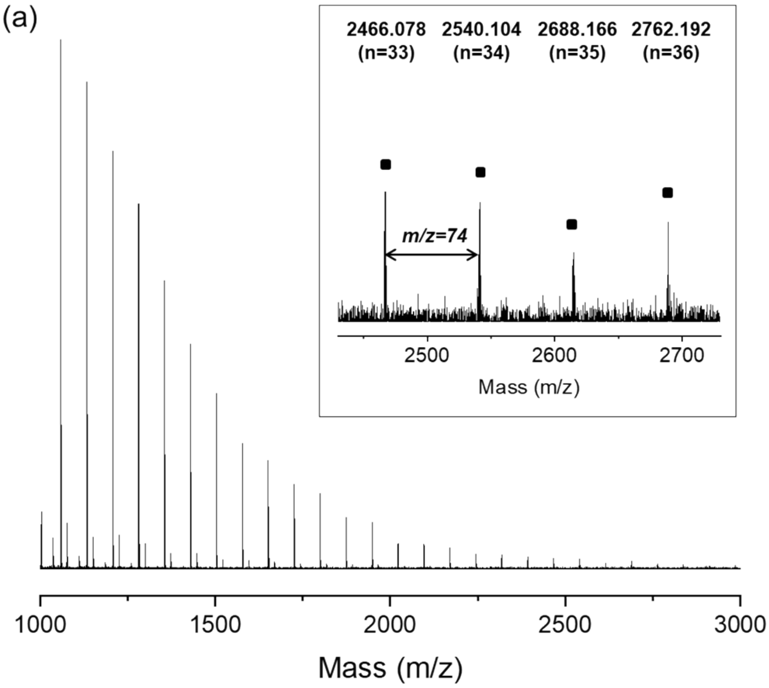


Figure S2. MALDI-ToF spectra of (a) polyglycerol (Table 1, Entry 1) (b) polyglycerol after N_3^- addition.

(a)



(b)

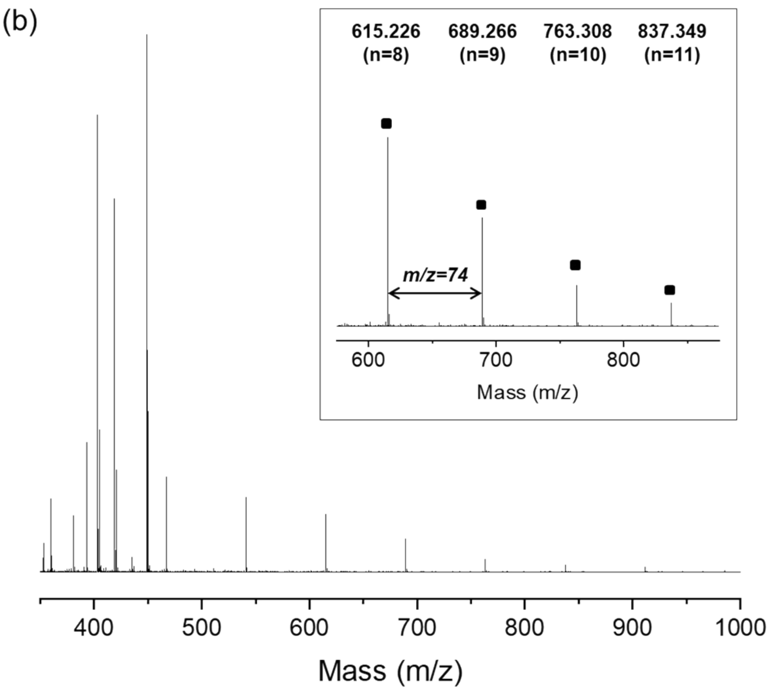
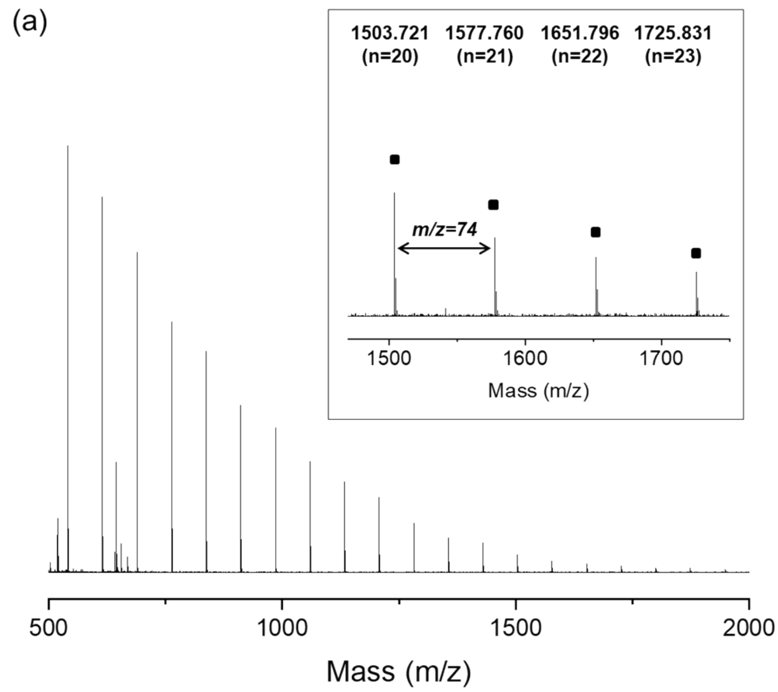


Figure S3. MALDI-ToF spectra of (a) polyglycerol (Table 1, Entry 2) (b) polyglycerol after N_3^- addition.



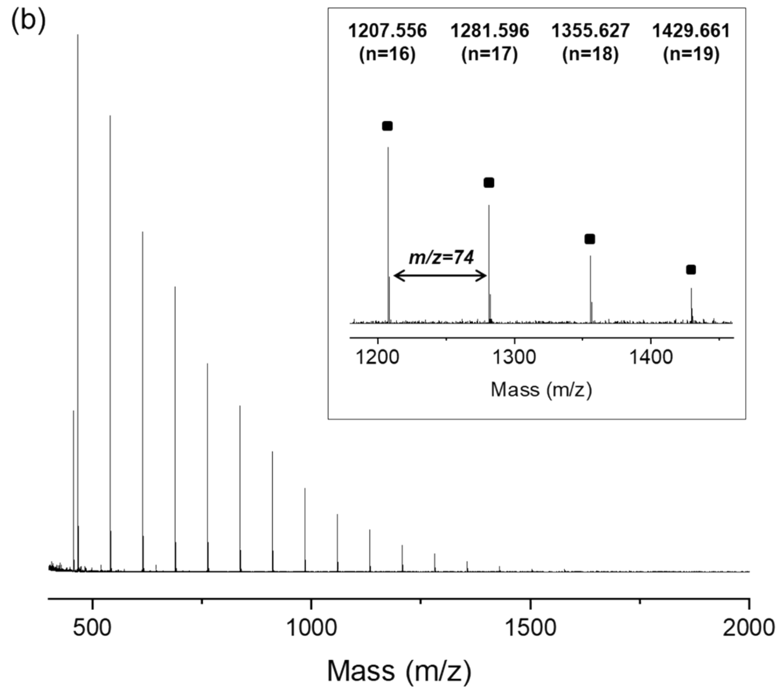


Figure S4. MALDI-ToF spectra of (a) polyglycerol (Table 1, Entry 3) (b) polyglycerol after N_3^- addition.

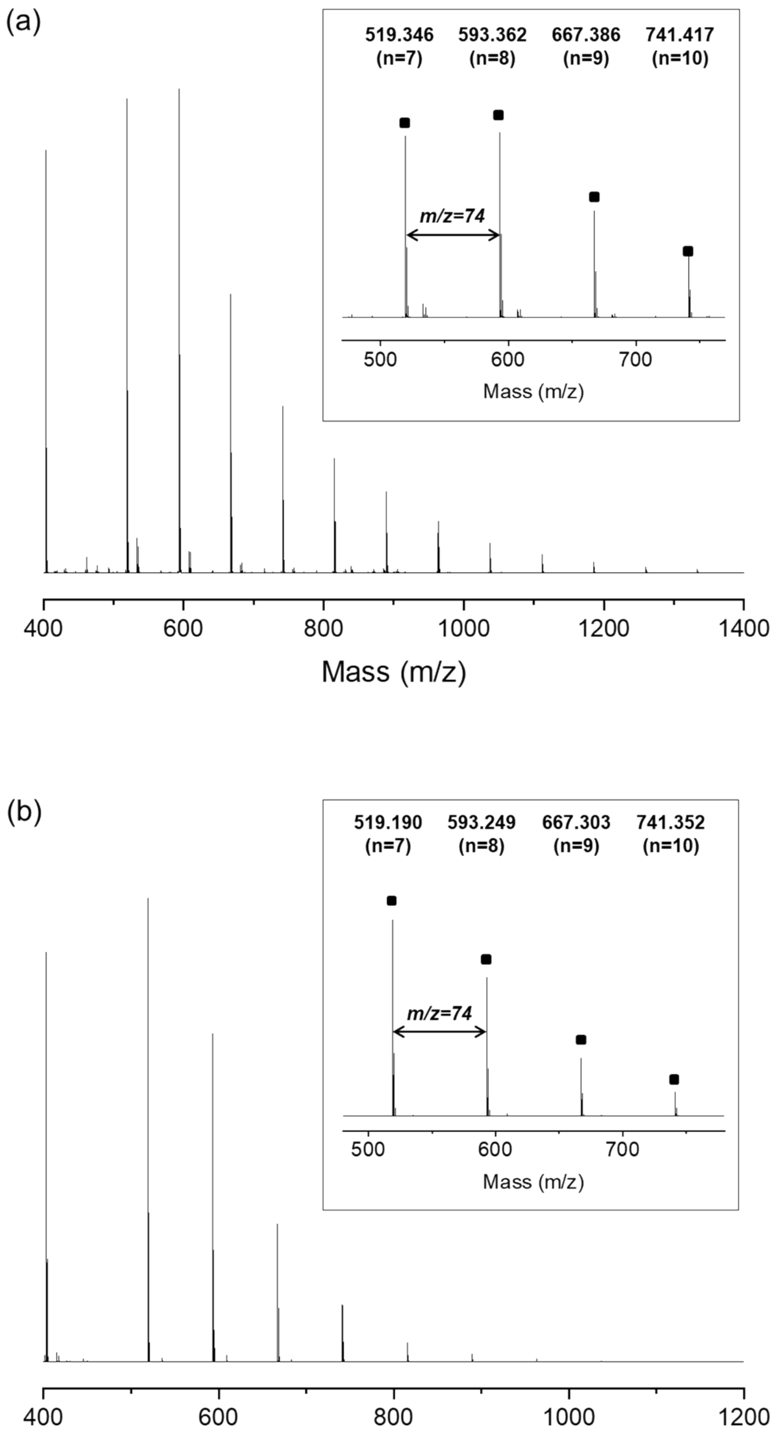
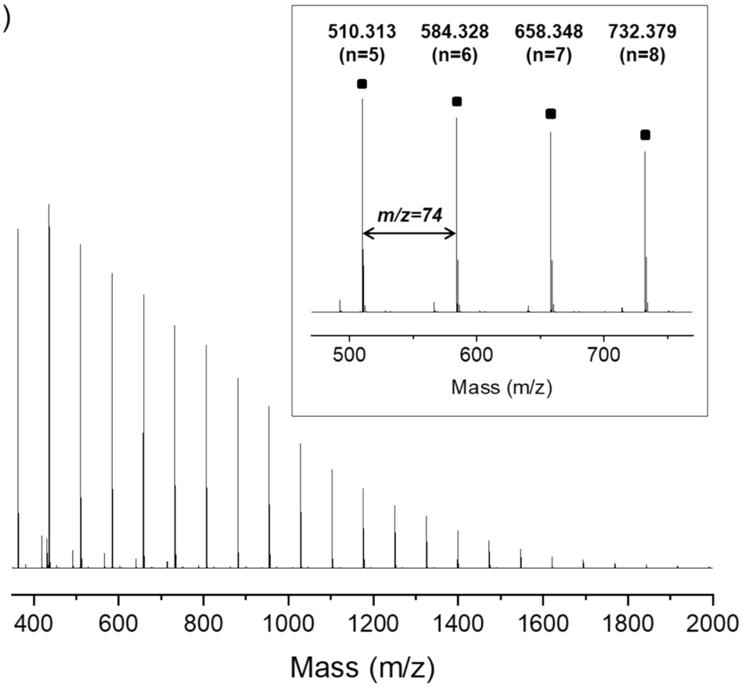


Figure S5. MALDI-ToF spectra of (a) polyglycerol (Table 1, Entry 4) (b) polyglycerol after N_3^- addition.

(a)



(b)

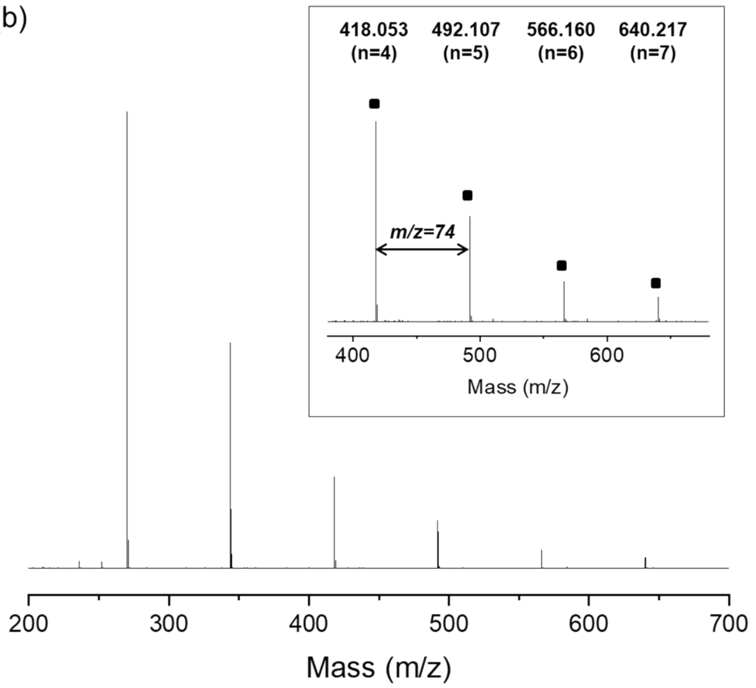


Figure S6. MALDI-ToF spectra of (a) polyglycerol (Table 1, Entry 5) (b) polyglycerol after N_3^- addition.

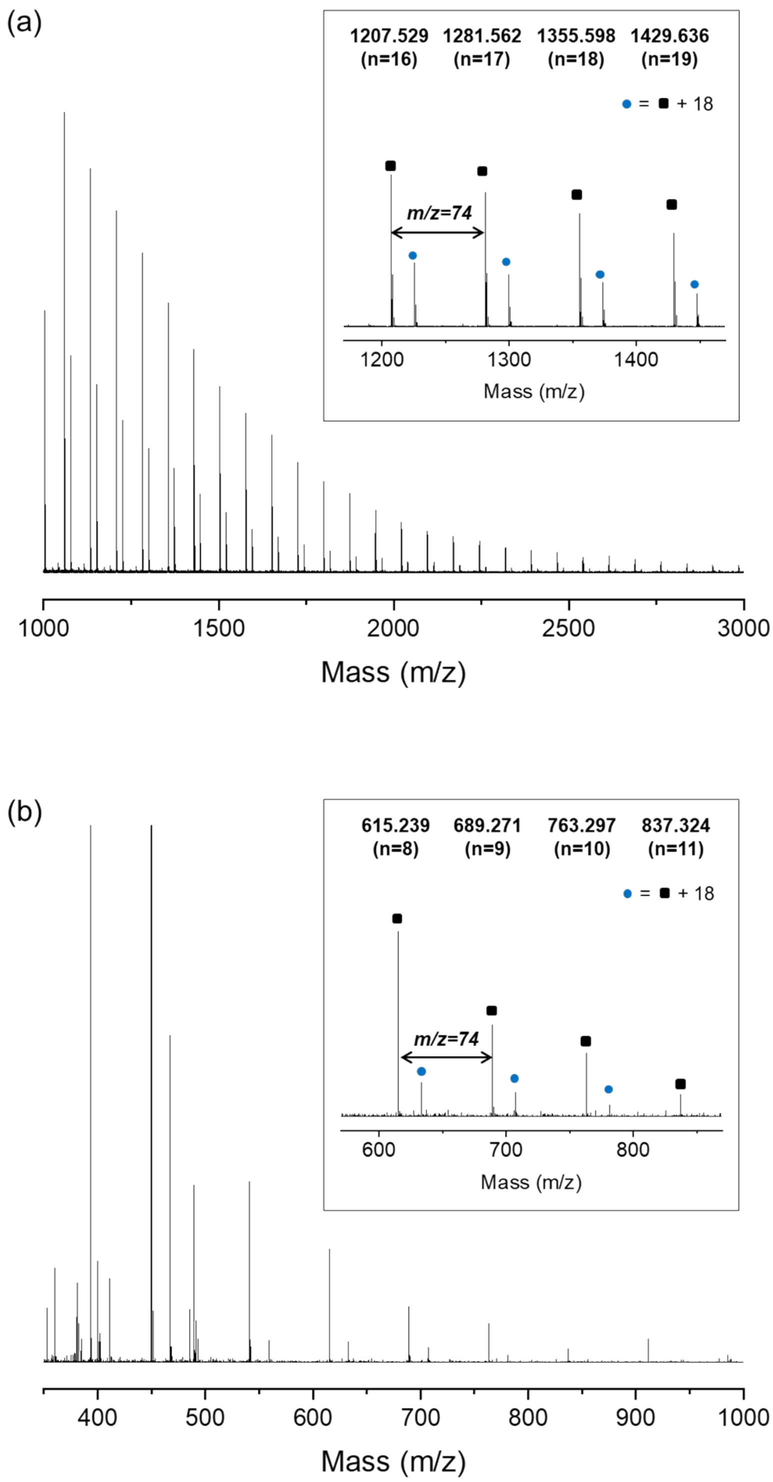


Figure S7. MALDI-ToF spectra of (a) polyglycerol (Table 1, Entry 8) (b) polyglycerol after N_3^- addition.

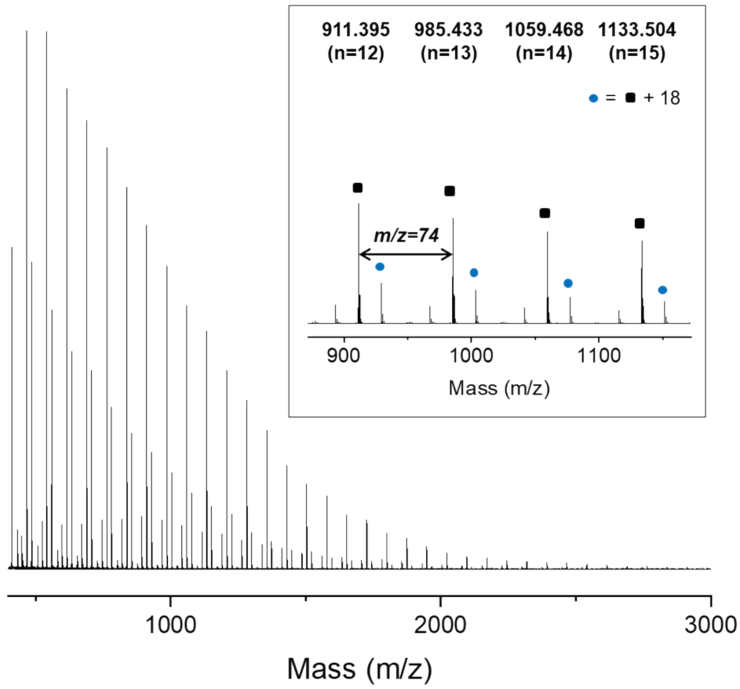


Figure S8. MALDI-ToF spectra of polyglycerol (Table 1, Entry 9).

IV. ^{1}H DOSY NMR spectra

Measurement: All ^{1}H DOSY spectra were acquired with the bipolar gradient pulse sequence using double stimulated echo and 3 spoil gradients for the convection compensation (dstebpgp3s). The time between pulses (Δ) was kept at 0.12 s, and the gradient length (δ) was set to 4 ms with the 5 ms of eddy current. MestReNova 12.0 was used for the processing of NMR data and the calculation of diffusion coefficient (*D*).

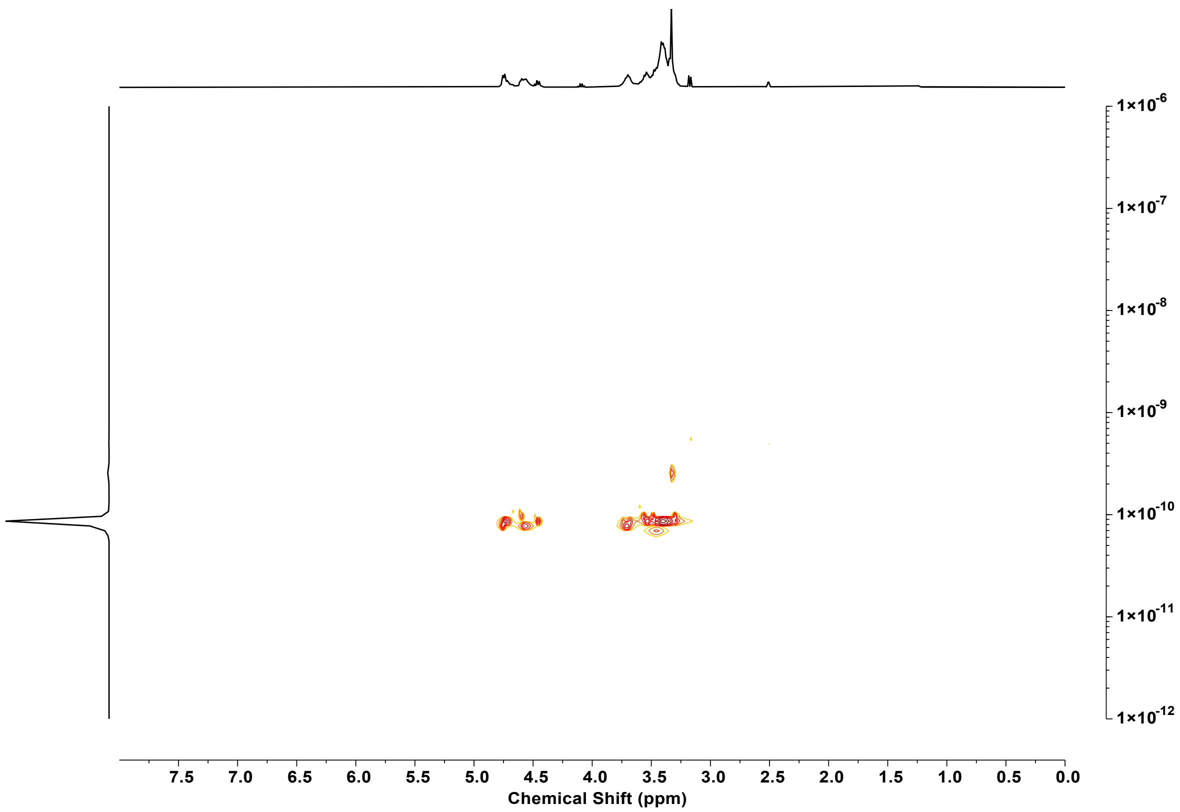


Figure S9. ^{1}H DOSY spectrum of entry 1(Table 1).

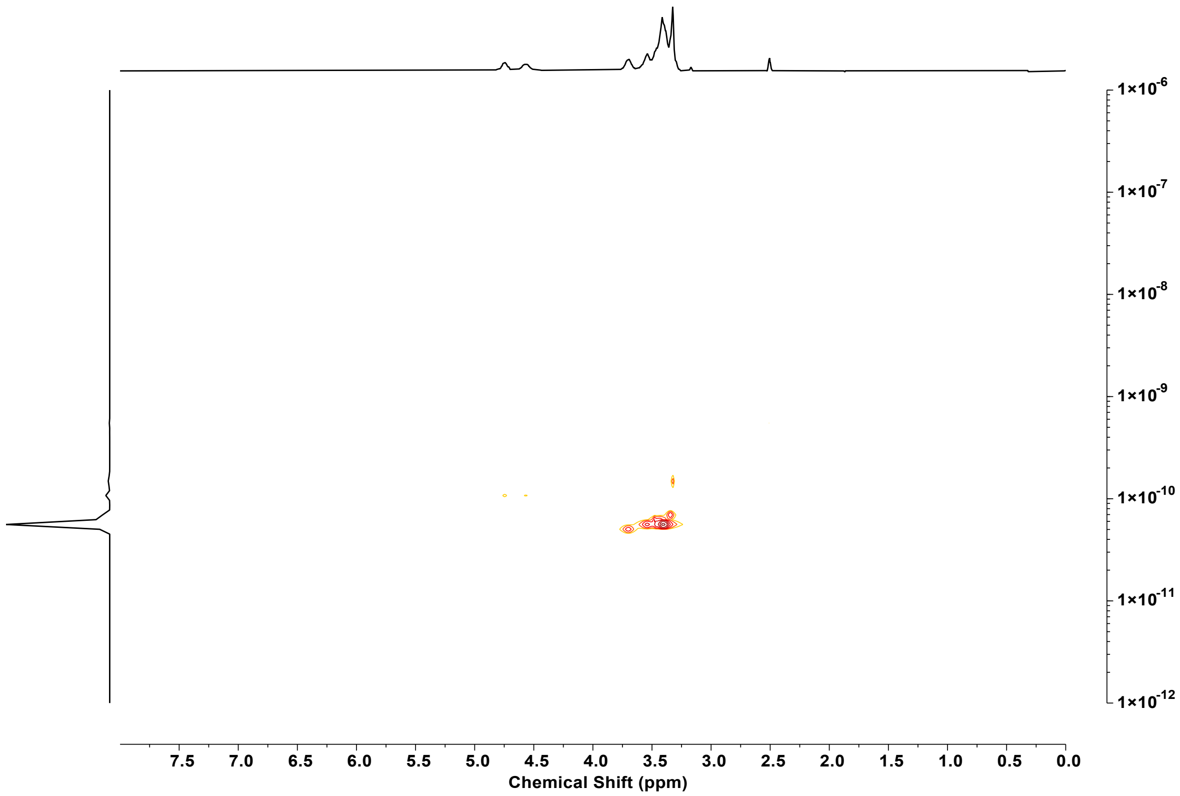


Figure S10. ^{1}H DOSY spectra of entry 2(Table 1).

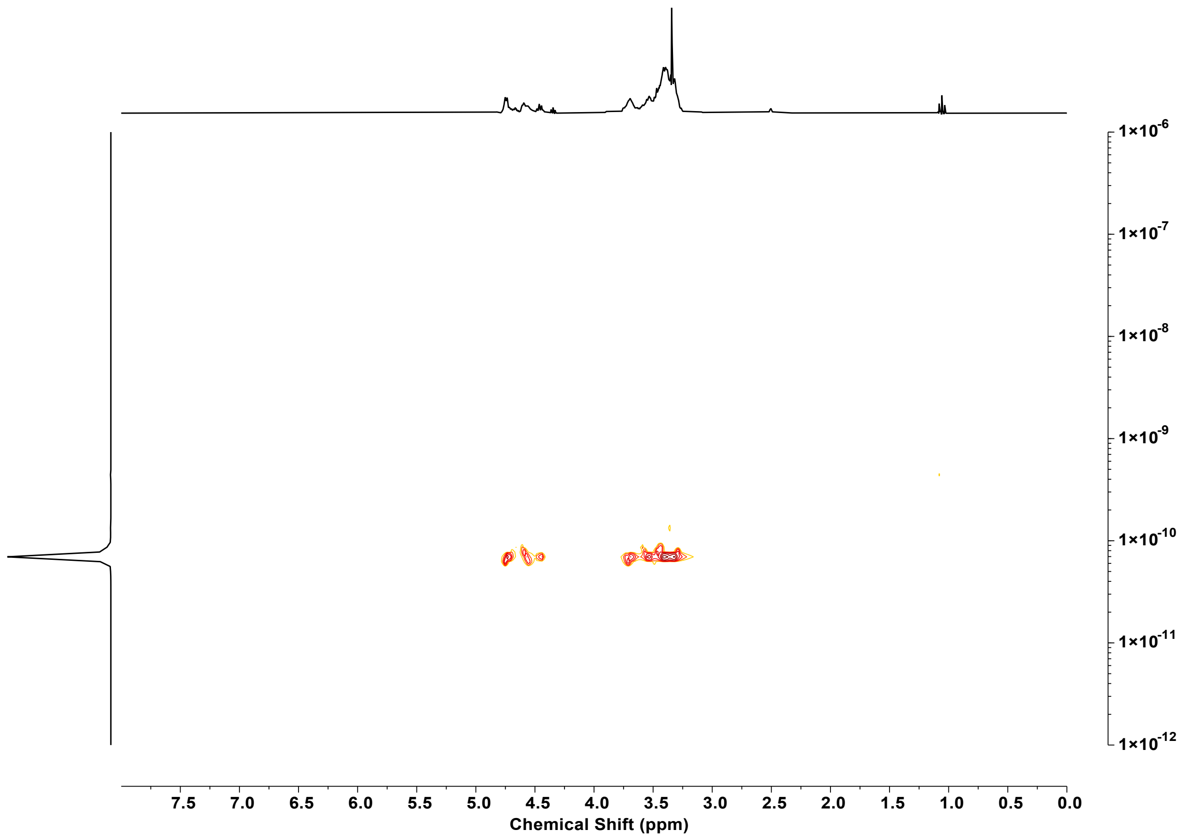


Figure S11. [1]H DOSY spectra of entry 3(Table 1).

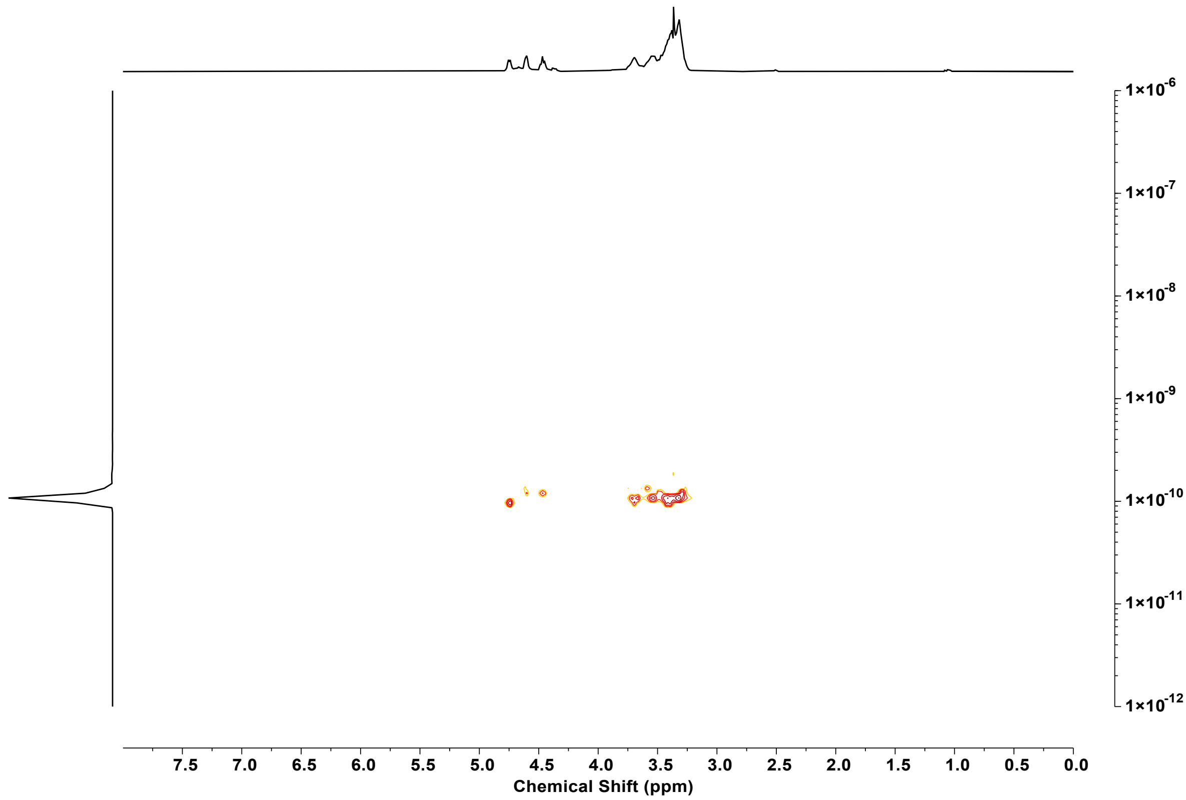


Figure S12. ^{1}H DOSY spectra of entry 4(Table 1).

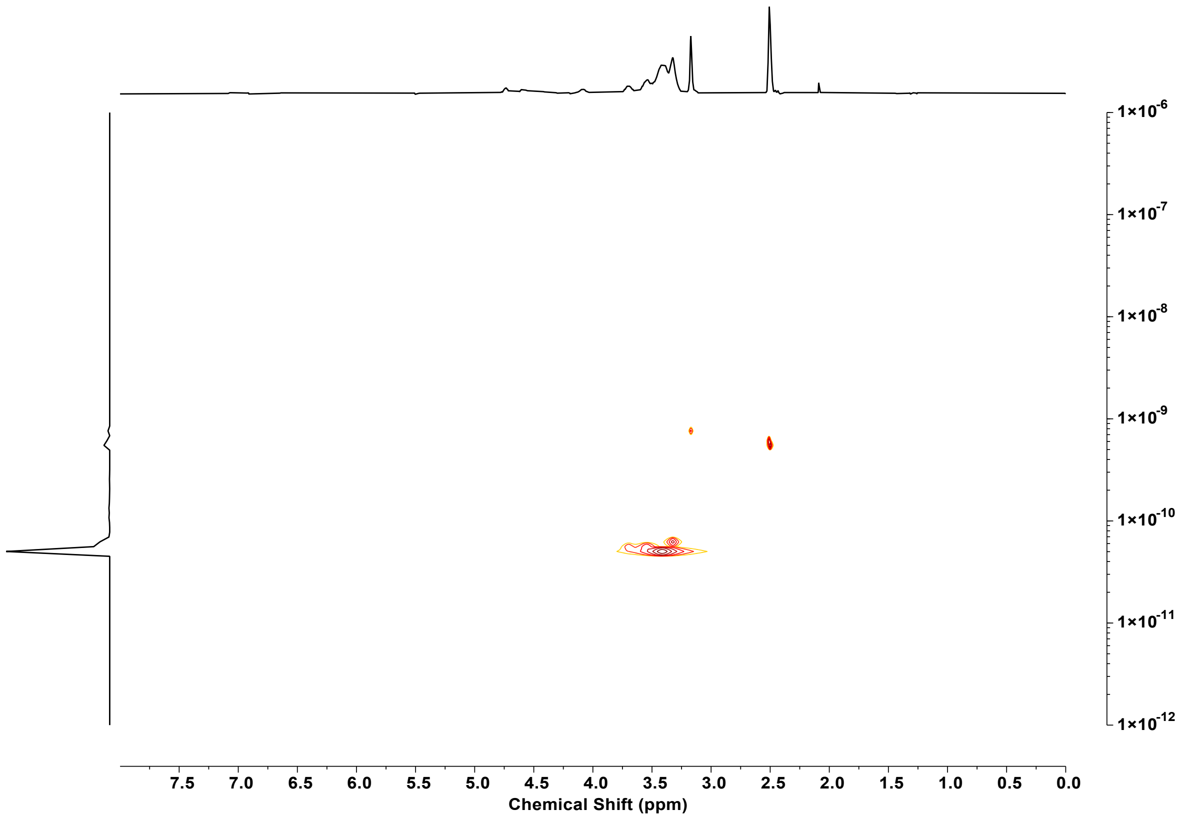


Figure S13. ^{1}H DOSY spectra of entry 5(Table 1).

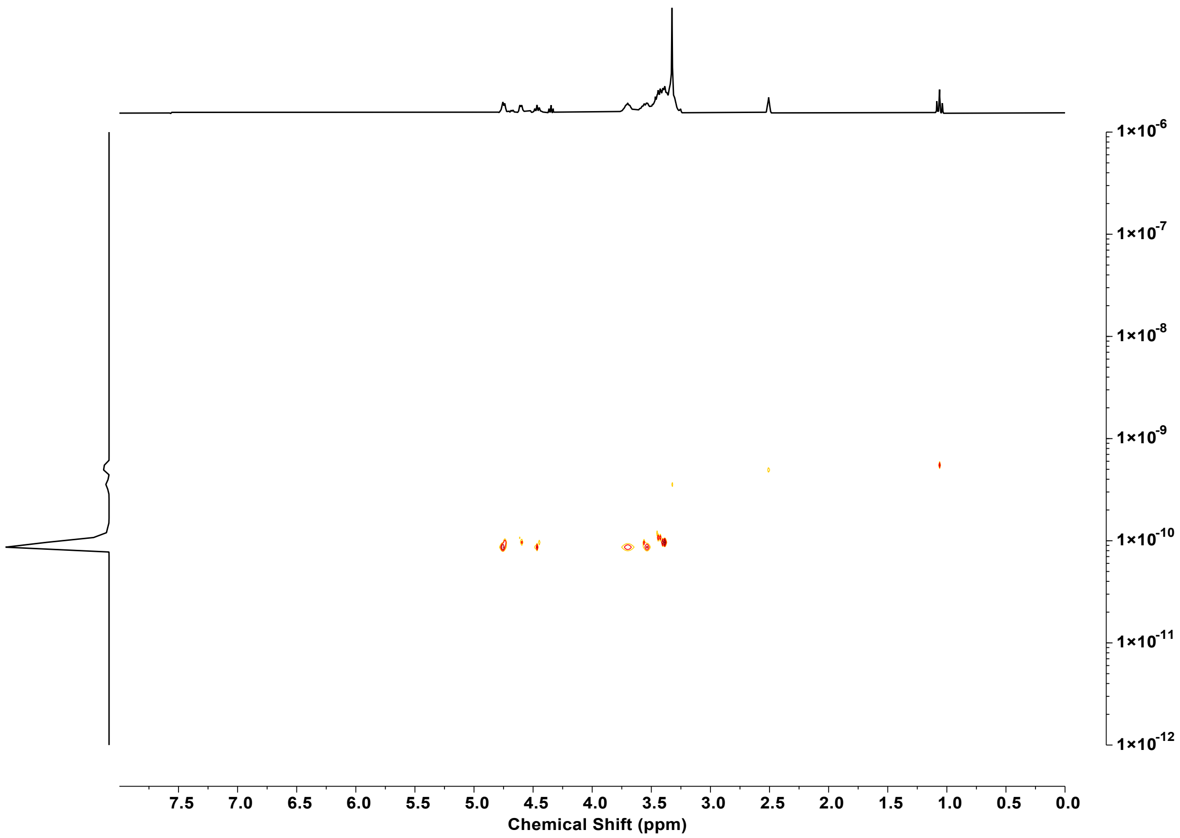


Figure S14. ^{1}H DOSY spectra of entry 8(Table 1).

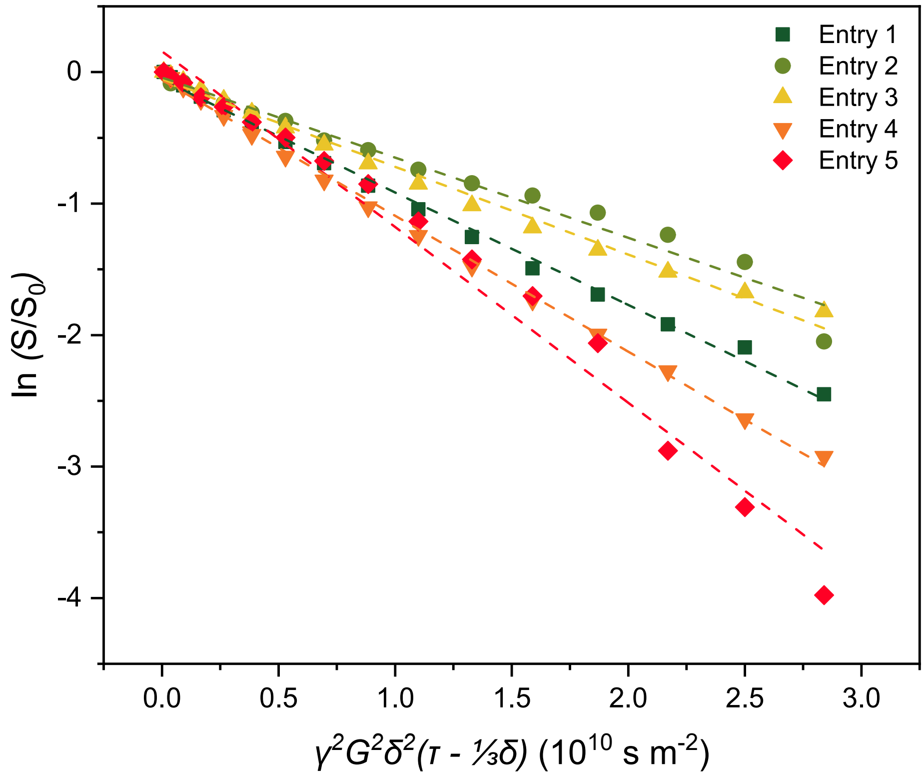
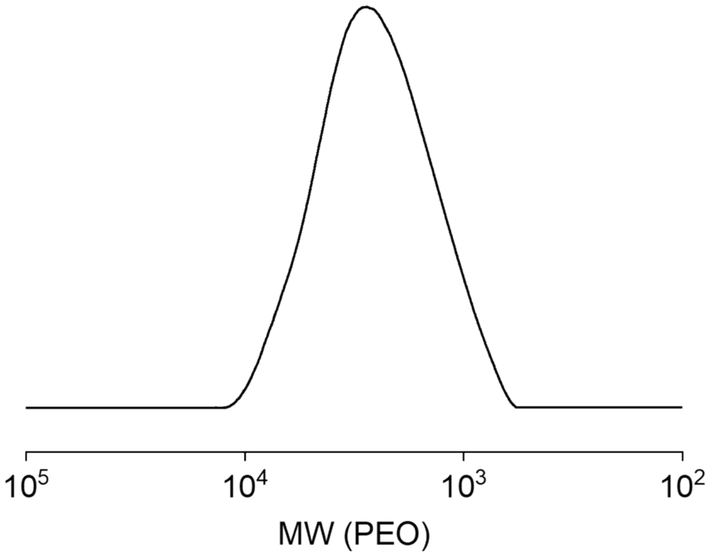


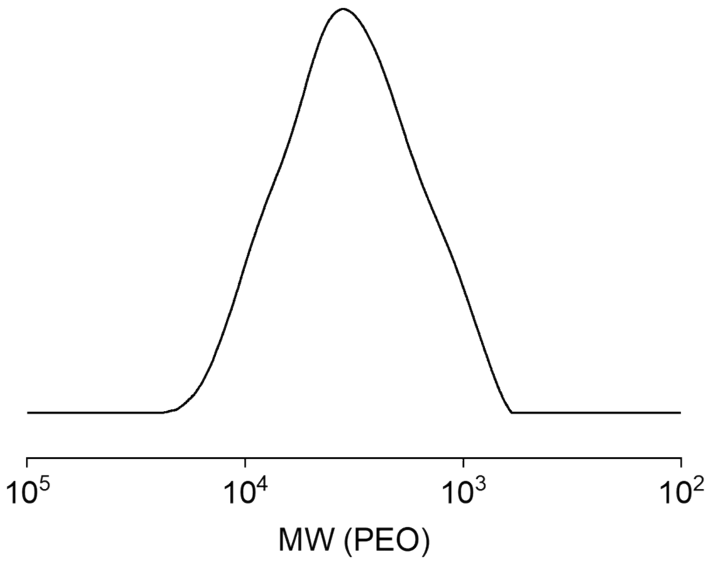
Figure S15. Stejskal-Tanner plot obtained from ^{1}H DOSY NMR (Table 1).

V. SEC data of polyglycerol



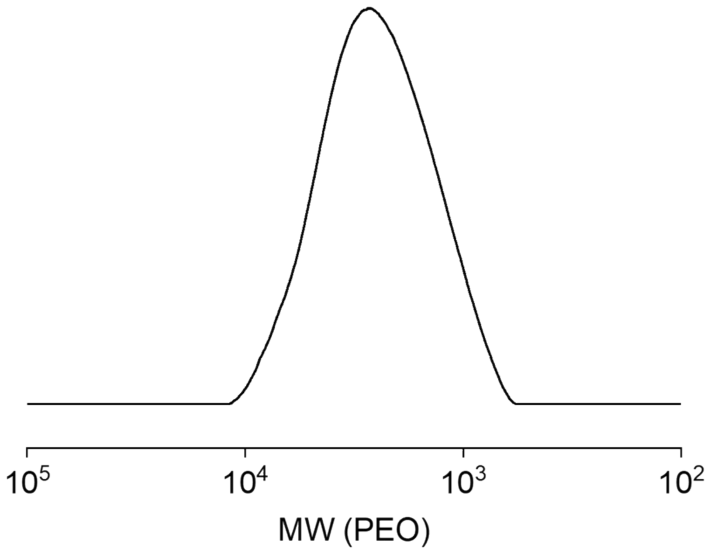
M_n: 2190, M_w: 3000, $Đ$: 1.37

Figure S16. GPC traces of polyglycerol (Table 1, Entry 1).



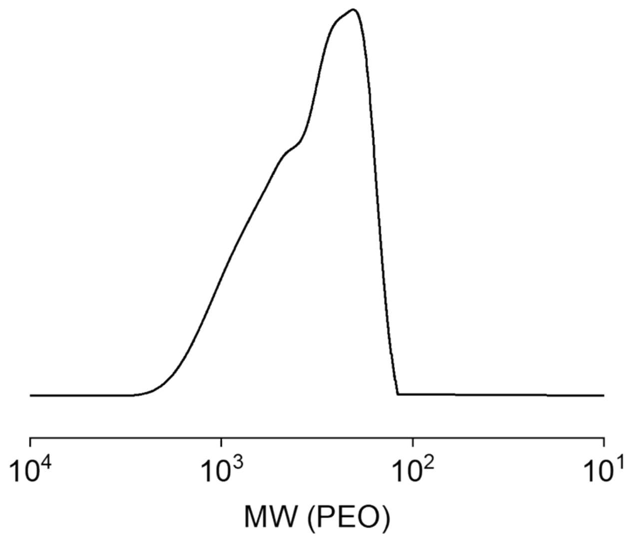
M_n: 2670, M_w: 4220, $Đ$: 1.59

Figure S17. GPC traces of polyglycerol (Table 1, Entry 2).



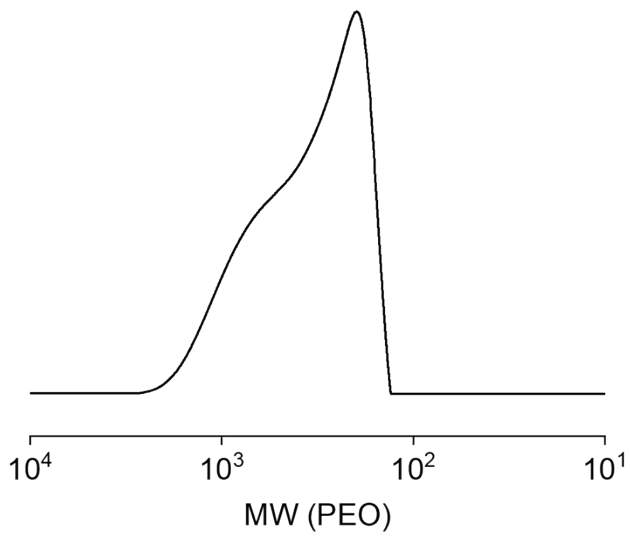
M_n: 2160, M_w: 2930, $Đ$: 1.36

Figure S18. GPC traces of polyglycerol (Table 1, Entry 3).



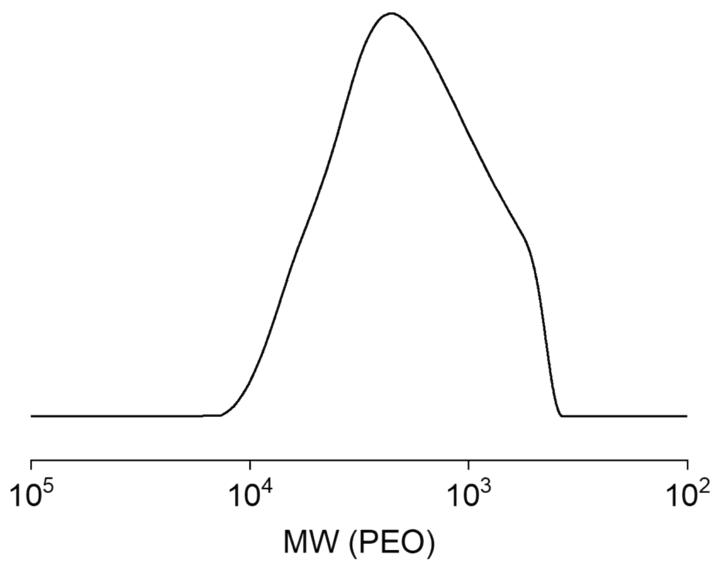
M_n: 640, M_w: 740, $Đ$: 1.12

Figure S19. GPC traces of polyglycerol (Table 1, Entry 4).



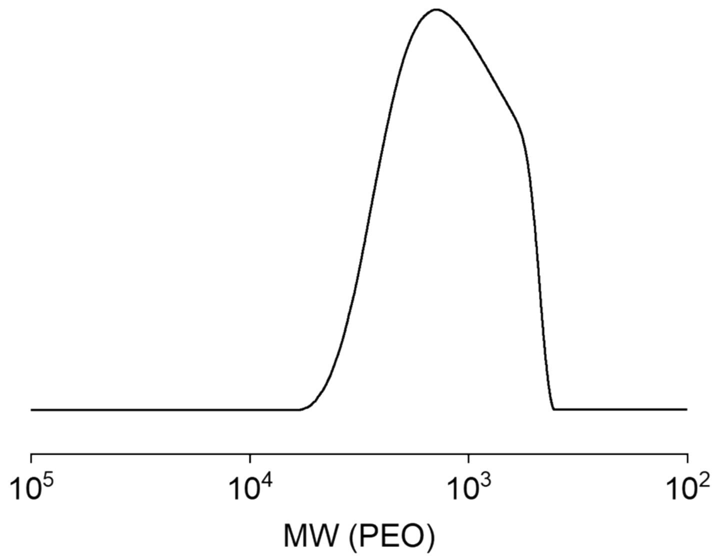
M_n: 680, M_w: 780, $Đ$: 1.15

Figure S20. GPC traces of polyglycerol (Table 1, Entry 5).



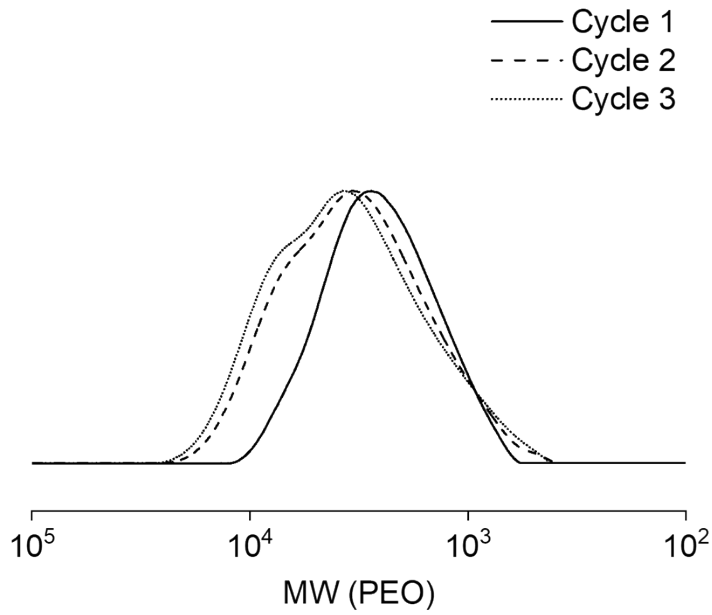
M_n: 1500, M_w: 2530, $Đ$: 1.69

Figure S21. GPC traces of polyglycerol (Table 1, Entry 8).



M_n: 1100, M_w: 1470, *Đ*: 1.33

Figure S22. GPC traces of polyglycerol (Table 1, Entry 9).



Cycle 2) M_n: 2570, M_w: 4290, *Đ*: 1.67

Cycle 3) M_n: 2670, M_w: 4690, *Đ*: 1.76

Figure S23. GPC traces of polyglycerol obtained from recycling experiments (Table 2).

VI. Inverse-gated ^{13}C NMR spectra of polyglycerol

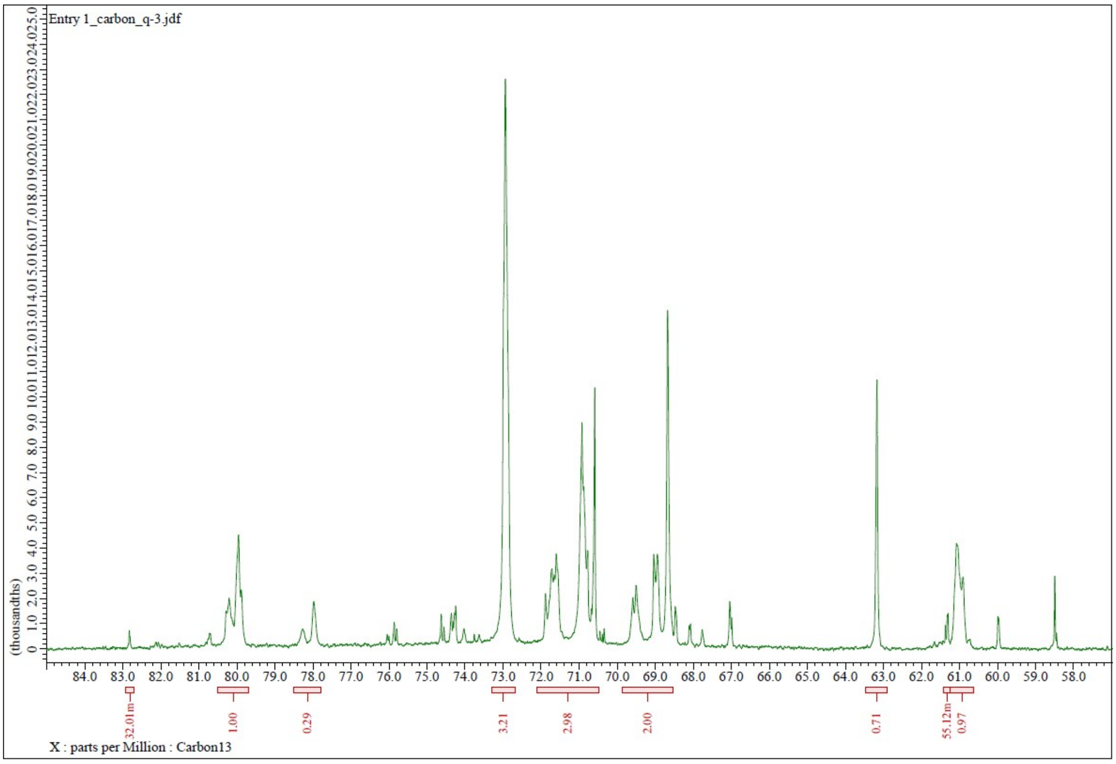


Figure S24. Inverse-gated ^{13}C NMR of entry 1 (Table 1)

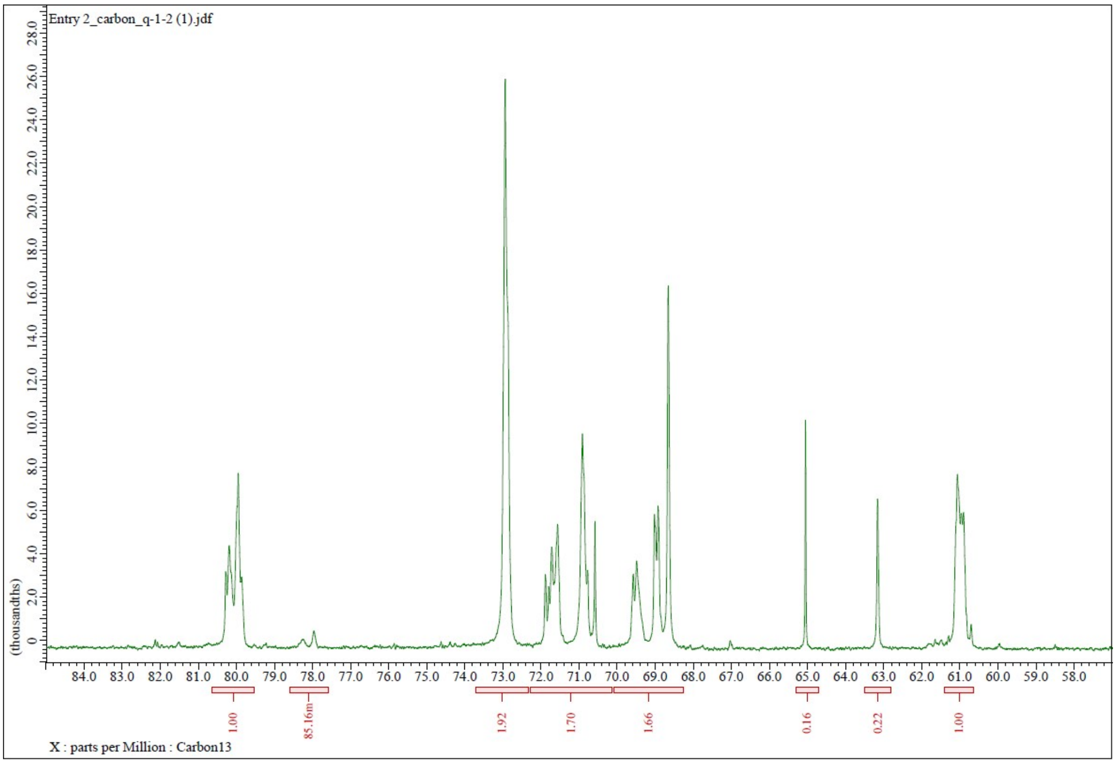


Figure S25. Inverse-gated ^{13}C NMR of entry 2 (Table 1)

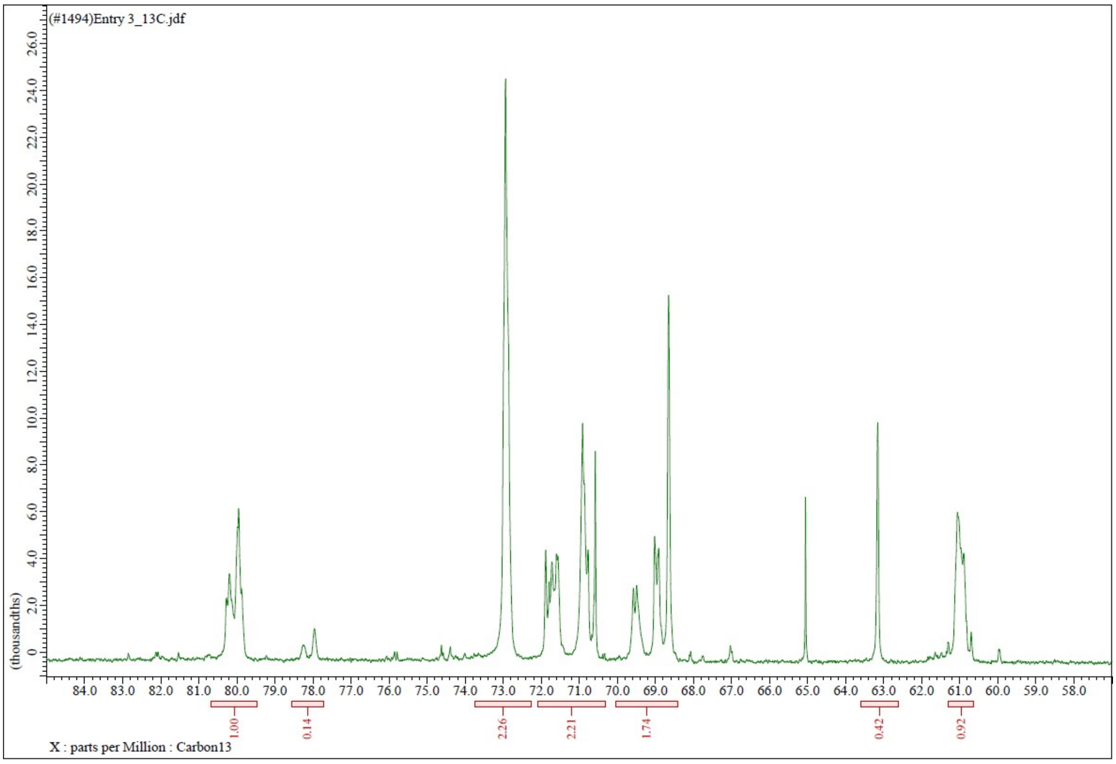


Figure S26. Inverse-gated ^{13}C NMR of entry 3 (Table 1)

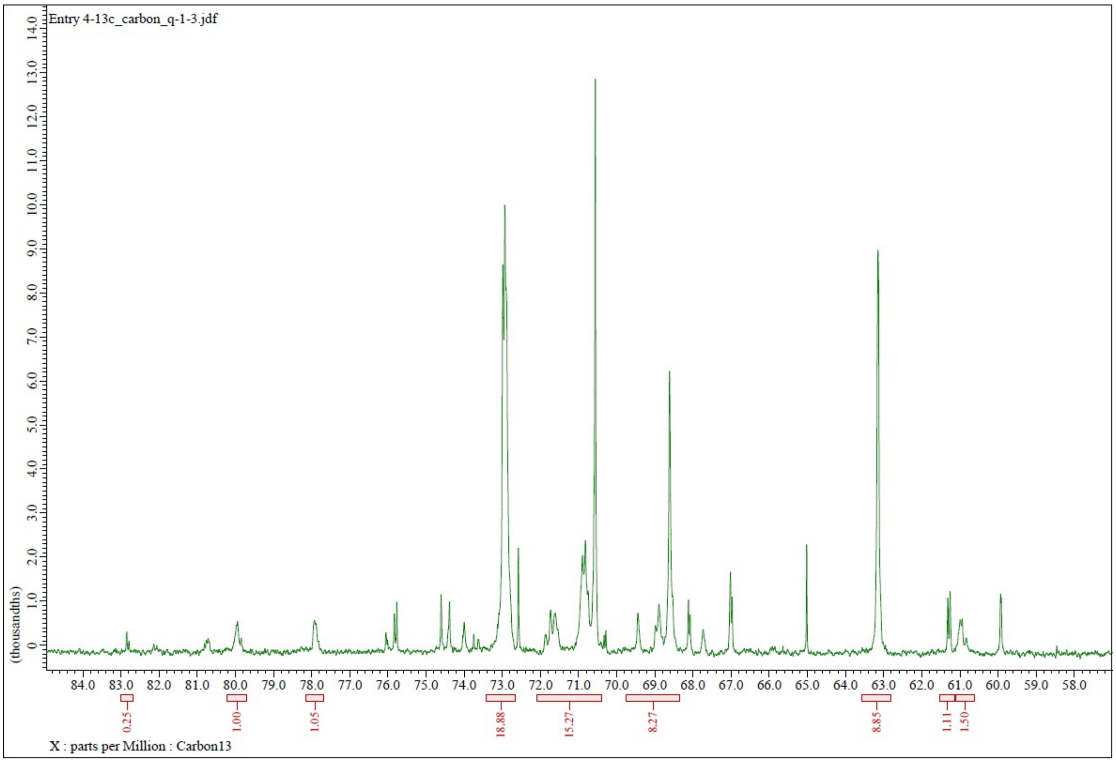


Figure S27. Inverse-gated ^{13}C NMR of entry 4 (Table 1)

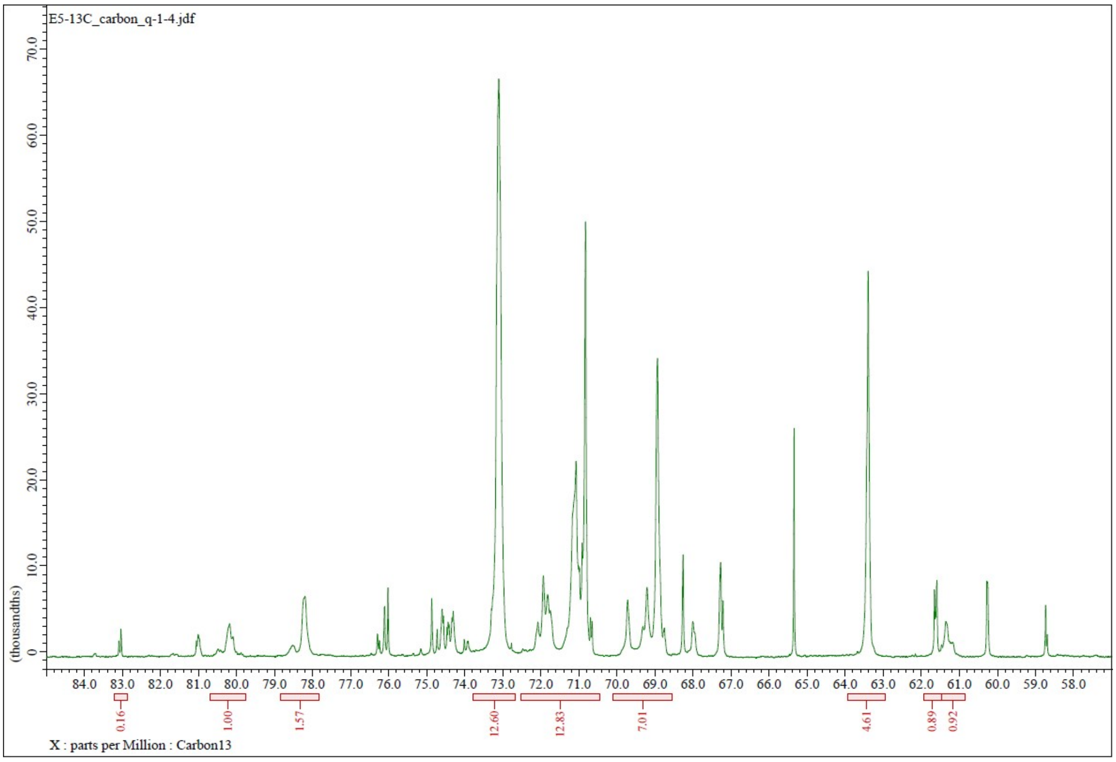


Figure S28. Inverse-gated ^{13}C NMR of entry 5 (Table 1)

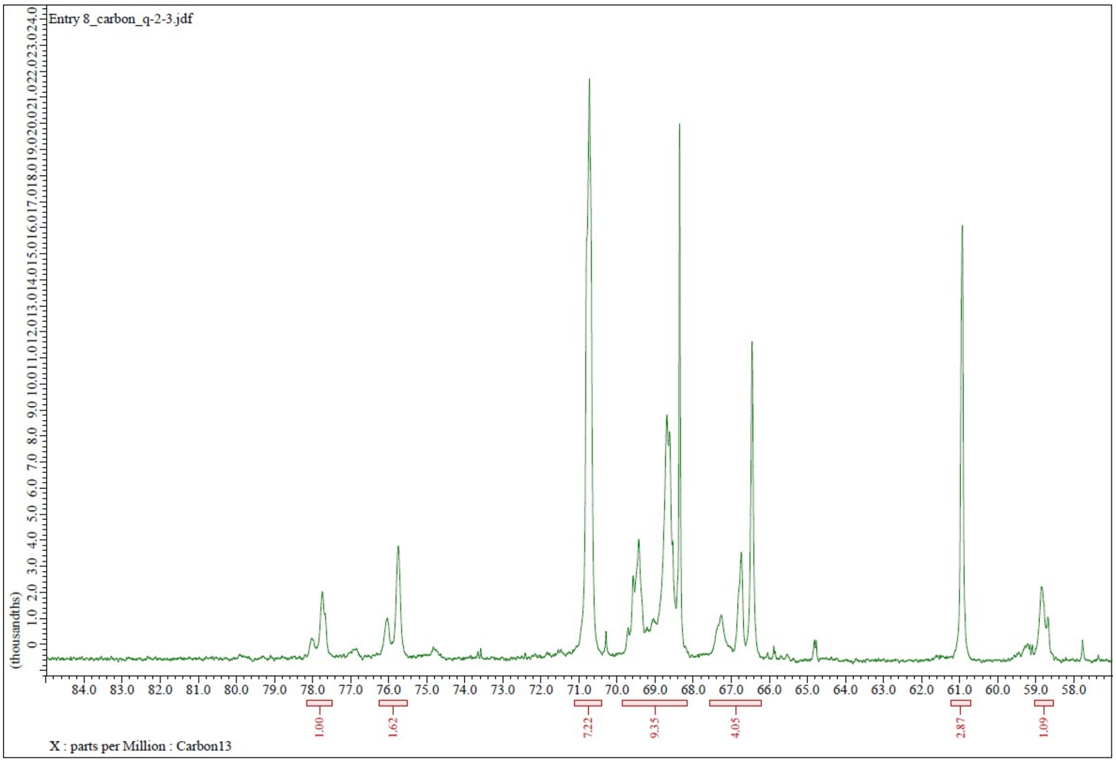


Figure S29. Inverse-gated ^{13}C NMR of entry 8 (Table 1)

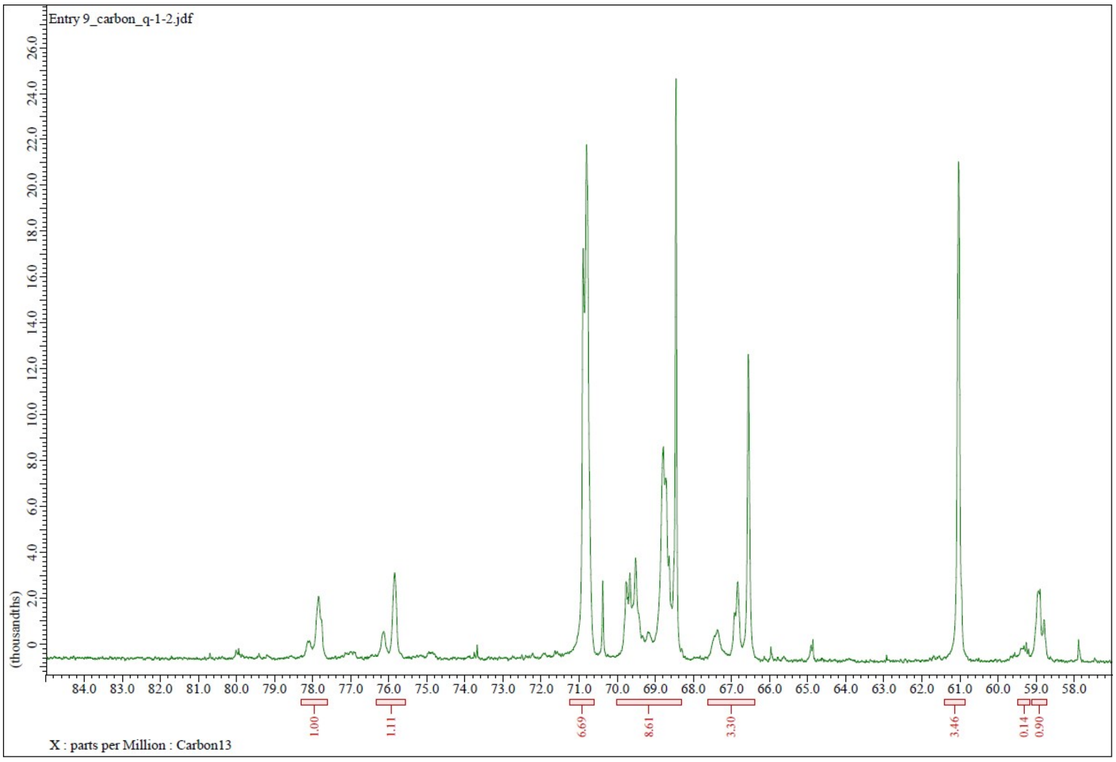


Figure S30. Inverse-gated ^{13}C NMR of entry 9 (Table 1)

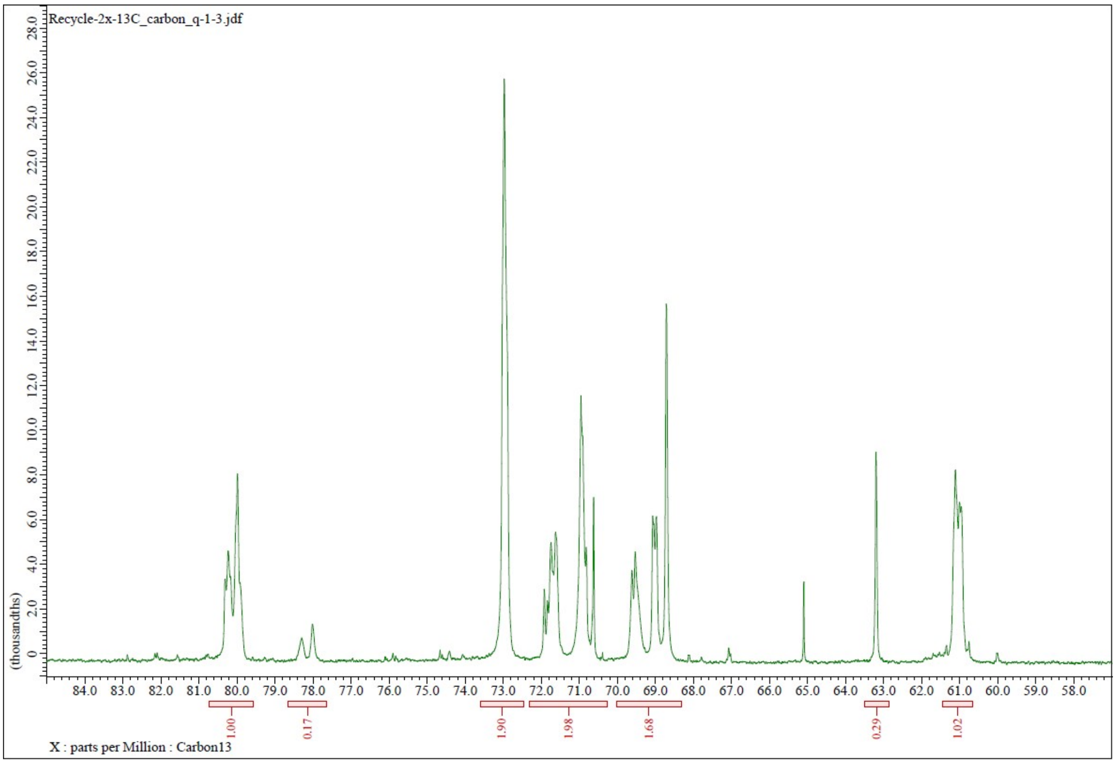


Figure S31. Inverse-gated ^{13}C NMR of polyglycerol obtained from 2nd cycle of recycling experiments (Table 2).

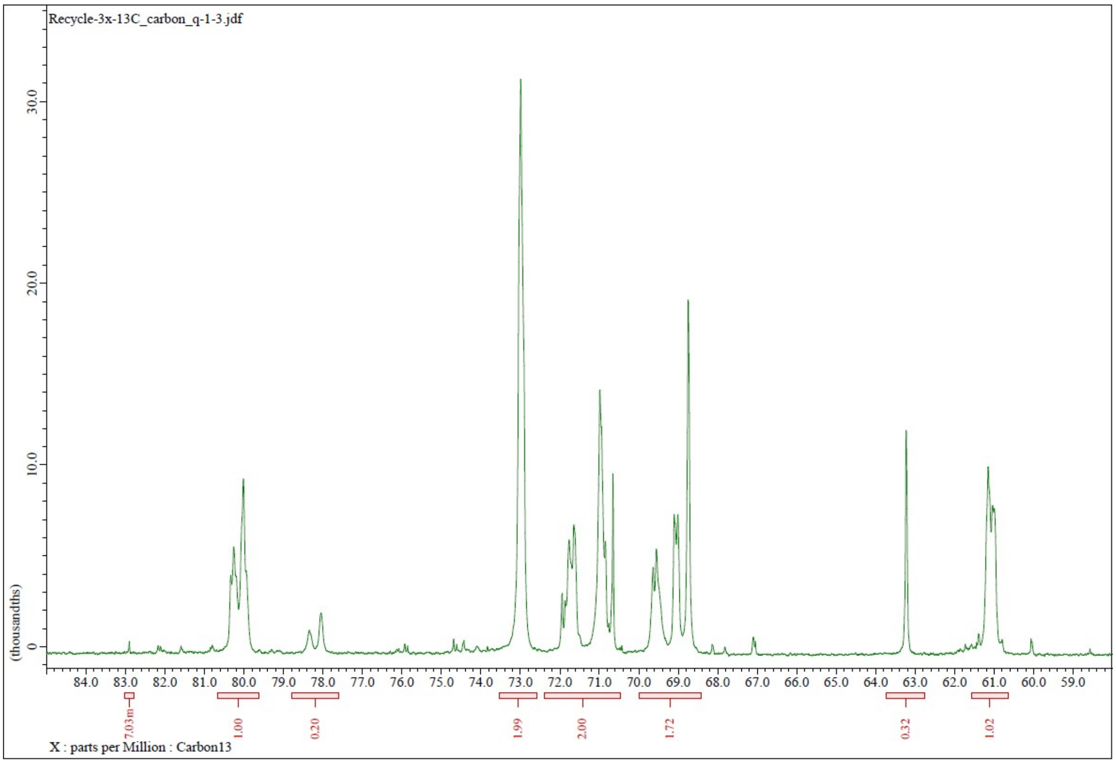


Figure S32. Inverse-gated ^{13}C NMR of polyglycerol obtained from 3rd cycle of recycling experiments (Table 2).

VII. Thermal analysis of polyglycerol

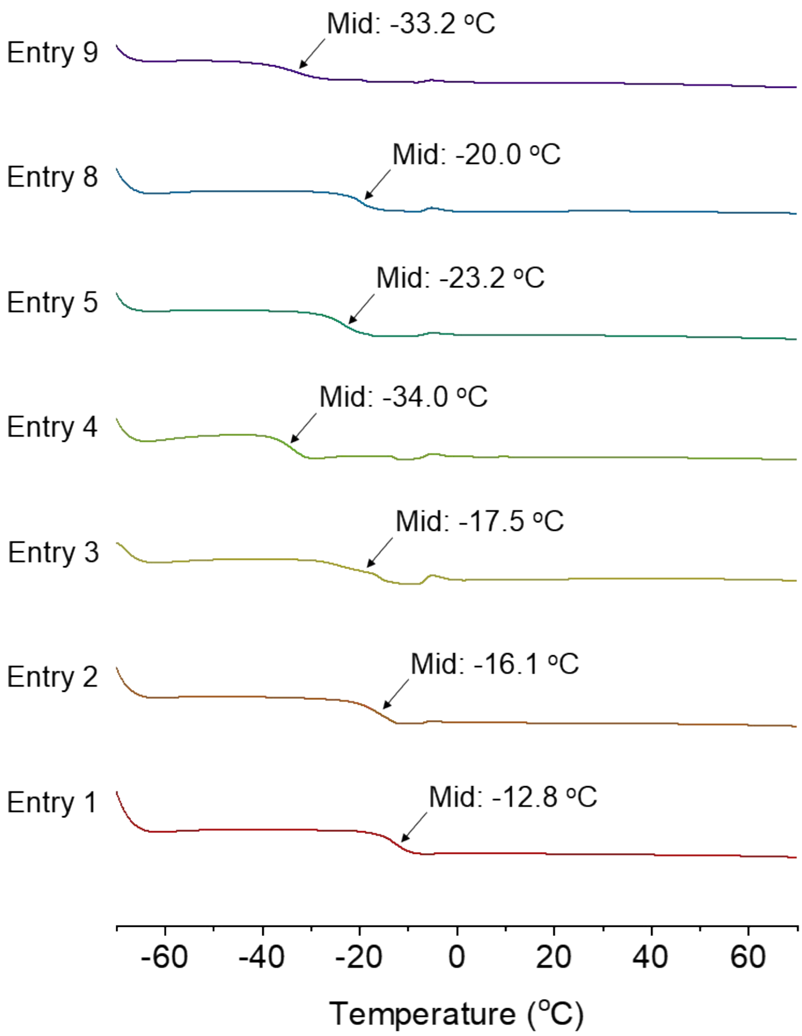


Figure S33. DSC curves of polyglycerol (Table 1).

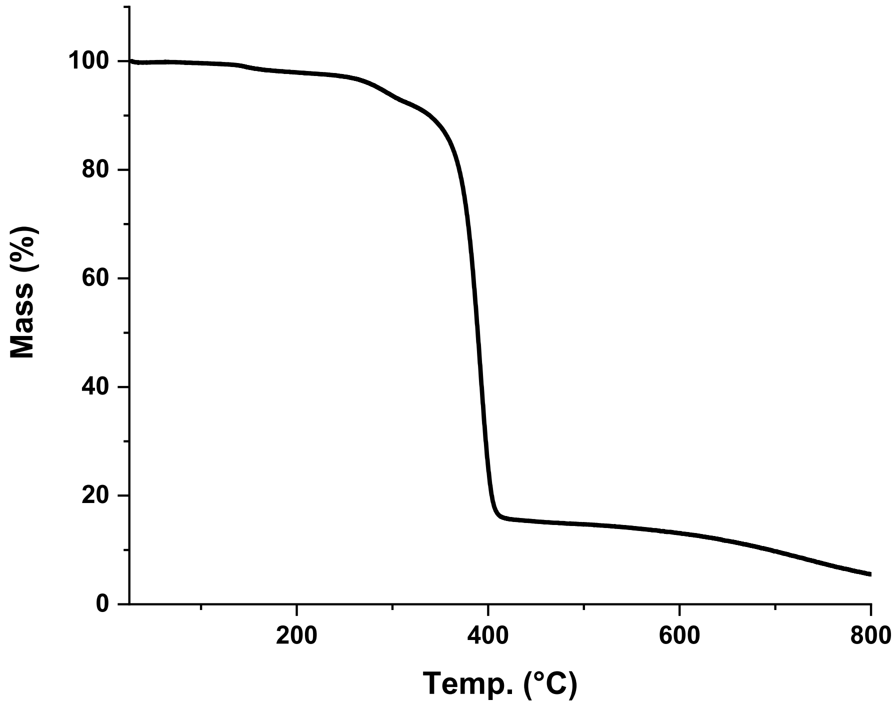


Figure S34. TGA curve of polyglycerol (Table 1, entry 1).

VIII. ^{1}H NMR and ESI-MS of the reaction mixture including copper catalysts

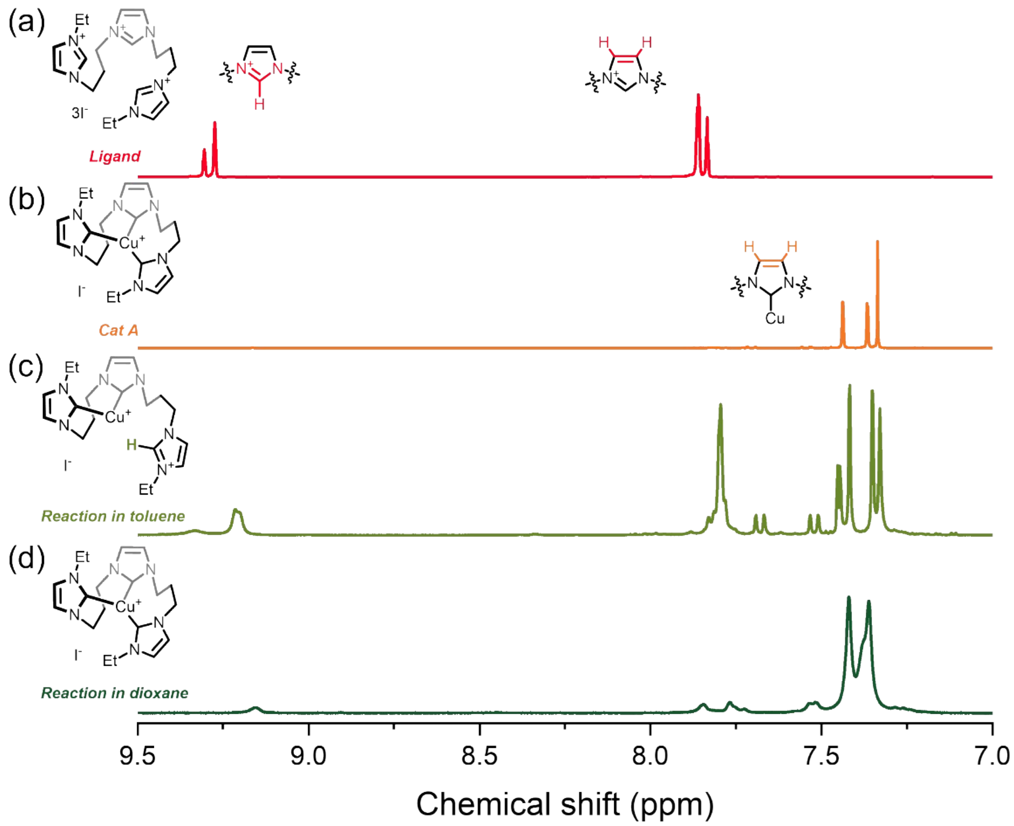


Figure S35. ^{1}H NMR spectra of (a) the ligand, (b) catalyst **A**, (c) the reaction mixture including catalyst **A** and glycidol in toluene, and (d) the reaction mixture including catalyst **A** and glycidol in dioxane

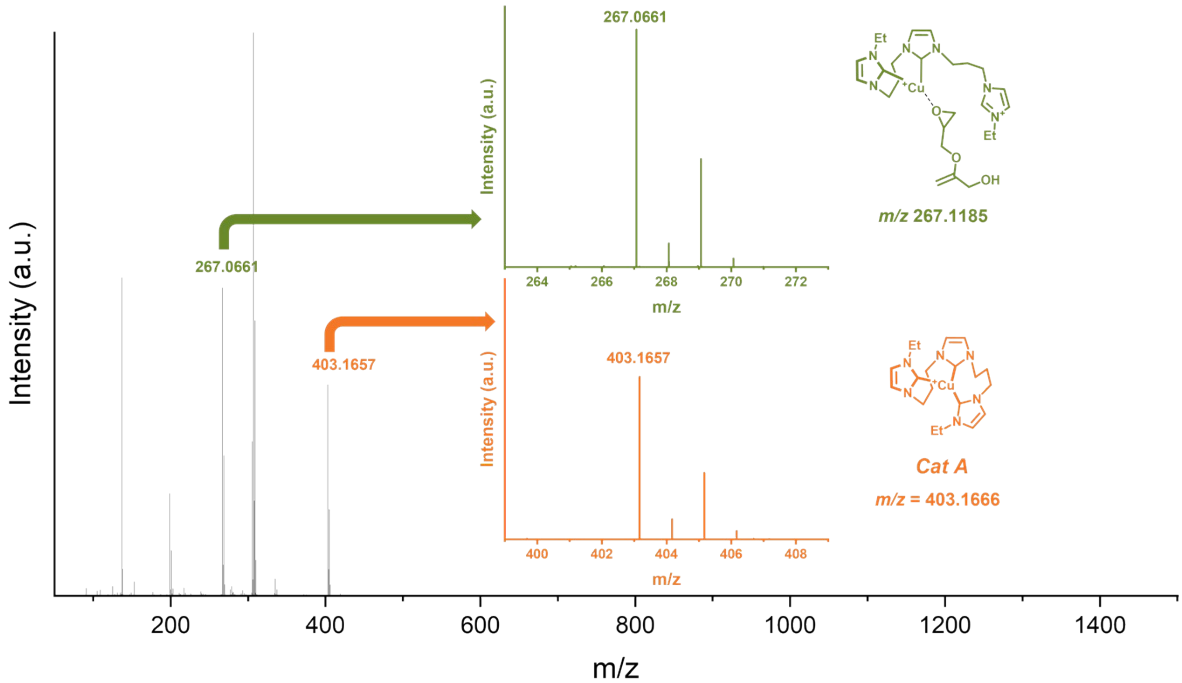


Figure S36. ESI-MS spectra of the reaction mixture including catalyst **A** and glycidol