Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Ductile Gas Barrier Poly(ester-amide)s Derived from Glycolide

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Materials:

Glycolide (Alasorb), Ethylene diamine (Fisher), 1,4-Diaminobutane (Sigma Aldrich), 1,6-Diaminohexane (Sigma Aldrich), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide•hydrochloride (Oakwood chemical), 4-Dimethylaminopyridine (Oakwood chemical) were purchased and used as received. Succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, sebacic acid were purchased from Sigma-Aldrich and recrystallized from acetone/water. Dichloromethane was obtained from Fisher Scientific and used after drying via the Pure Process Technology Glass Contour Solvent Purification System (Solvent Column). 1,1,1,3,3,3-Hexafluoro-2-isopropanol was purchased from Oakwood chemical and used as received.

Characterization Methods:

^{1}H NMR and ^{13}C NMR spectra were obtained from Bruker Advance III HD 400MHz Spectrometer and Bruker Advance III HD 500MHz. Molar mass of poly(ester-amide)s were estimated using a size exclusion chromatography (SEC) with HFIP (0.35 mL.min^{-1} at 40 °C) using an EcoSEC system HLC-8240GPC series liquid chromatograph. Size exclusion was conducted with two Tosoh TSKgel SuperAWM-H. Chromatograms were collected using a refractive index detector and. Molecular masses and dispersity were reported by conventional calibration vs. polymethyl methacrylate (PMMA) standards. The polymer solutions were filtered through a 0.2 μm filter (Whatman) before injection into the column. Fourier transform infrared (FTIR) spectra were obtained using a Bruker Alpha Platinum ATR-FTIR instrument with a diamond single bounce crystal. Differential scanning calorimetry (DSC) was recorded on a TA Instruments Q-1000 DSC using hermetically sealed aluminum Tzero pans under nitrogen with heating and cooling rate of 10 °C/min. Thermogravimetric analysis (TGA) was recorded on a TA Instruments Q500 under

nitrogen atmosphere at a heating rate of 10 °C.min^{-1}. WAXS experiments were performed at the Sector 5 of the Advanced Photon Source at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) at Argonne National Laboratory. Polymer films to measure mechanical properties and gas permeability were obtained using Compact Tape Casting Coater and Doctor Blade-MSK-AFA-H200A at room temperature. Mechanical properties were recorded using Shimadzu Autograph AGS-X Tensile Tester. Oxygen transmission rates of the films were measured with OxTran (Mocon, USA) according to ASTM D3985-02 standard at 0% humidity level with oxygen gas at atmospheric pressure and 23 °C test temperature. The carrier gas was 98% of nitrogen gas and 2% of hydrogen gas. The films of TOC measurements were prepared using Compact Tape Casting Coater with around 0.2 mm thickness. The resulting films were dried overnight at ambient conditions and overnight under vacuum. The films were punched out using a circular die cut (9 mm inner diameter). TOC measurements were performed using a Shimadzu TOC-L analyzer. 50 µL aliquots at various time points were diluted with 9950 µL DI water. The single crystal diffraction data were obtained using a Bruker PHOTON-III diffractometer at 125 K using MoKα radiation (parabolic mirrors) with a frame time of 30 seconds and a detector distance of 5.0 cm. The intensities were corrected for absorption and decay (SADABS). The crystal structures were solved and refined using SHELXT 2014/5 (Sheldrick, 2014) and SHELXL-2018/3 (Sheldrick, 2018), respectively.

Synthetic methods:

*Synthesis of N,N'-(ethane-1,2-diyl)bis(2-hydroxyacetamide) (**2G**):* In a 100 ml round bottom flask, ethylene diamine (5.5 ml, 82 mml) was stirred at 0 °C and glycolide (9.5 g, 82 mml) was slowly added, then warm up to room temperature. After reaction is completed, the crude product was

purified by recrystallization from acetone and water to afford the **2G** as yellowish solid (11 g, 78%). ^{1}H NMR (500 MHz, DMSO-*d*) δ 7.86 (s, 2H), 5.48 (s, 2H), 3.78 (s, 4H), 3.23 – 3.14 (m, 4H). ^{13}C NMR (125 MHz, DMSO-*d*) δ 172.2, 61.4, 38.2.

*Synthesis of N,N'-(butane-1,4-diyl)bis(2-hydroxyacetamide) (**4G**):* In a 100 ml round bottom flask, 1,4-diaminobutane (7.6 g, 86 mmol) was stirred at 40 °C and glycolide (10 g, 86 mmol) was slowly added. After reaction is completed, the crude product was purified by recrystallization from acetone and water to afford the **4G** as white solid (14 g, 80% yield). ^{1}H NMR (500 MHz, DMSO-*d*) δ 7.70 (t, *J* = 6.0 Hz, 2H), 5.43 (s, 2H), 3.77 (s, 4H), 3.10 – 3.06 (m, 4H), 1.40 – 1.37 (h, *J* = 3.3 Hz, 4H). ^{13}C NMR (125 MHz, DMSO-*d*) δ 171.6, 61.4, 37.7, 26.8.

*Synthesis of N,N'-(hexane-1,6-diyl)bis(2-hydroxyacetamide) (**6G**):* In a 500 ml round bottom flask, 1,6-diaminohexane (50 g, 434 mmol) was stirred at 60 °C and glycolide (50 g, 434 mmol) was slowly added. After reaction is completed (30 min), the crude product was purified by recrystallization from acetone and water to afford the **6G** as white solid (75 g, 75% yield). ^{1}H NMR (500 MHz, DMSO-*d*) δ 7.67 (t, *J* = 6.1 Hz, 2H), 5.41 (t, *J* = 5.8 Hz, 2H), 3.77 (d, *J* = 5.7 Hz, 4H), 3.07 (dt, *J* = 7.2, 6.2 Hz, 4H), 1.50 – 1.34 (m, 4H), 1.25 – 1.22 (m, 4H). ^{13}C NMR (125 MHz, DMSO-*d*) δ 171.5, 61.4, 37.9, 29.2, 26.1.[1]

General procedures for the synthesis of poly(ester-amide)s: A round bottom flask was charged with diamidodiol (11 mmol), diacid (11 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide•hydrochloride (6.2 g, 32 mmol), and 4-

dimethylaminopyridine (0.9 g, 6 mmol) under an argon atmosphere. Dichloromethane (32 ml) was added at room temperature under Ar. The reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was diluted with 1,1,1,3,3,3-hexafluoroisopropanol, precipitated in methanol twice and dried for a minimum of 1 day at room temperature in a vacuum oven.

^{1}H NMR and ^{13}C NMR characterization of poly(ester-amide)s:

6G-2

^{1}H NMR (400 MHz, TFA-*d*) δ 4.97 (s, 4H), 3.51 (t, *J* = 7.6 Hz, 4H), 3.00 (s, 4H), 1.72 (bs, 4H), 1.49 (bs, 4H). ^{13}C NMR (100 MHz, TFA-*d*) δ 176.3, 173.2, 64.6, 42.8, 30.4, 30.3, 28.0.

6G-3

^{1}H NMR (400 MHz, TFA-*d*) δ 4.84 (s, 4H), 3.39 (t, *J* = 7.3 Hz, 4H), 2.63 (t, *J* = 7.3 Hz, 4H), 2.07 (t, *J* = 7.3 Hz, 2H), 1.60 (s, 4H), 1.37 (s, 4H). ^{13}C NMR (100 MHz, TFA-*d*) δ 177.4, 173.2, 64.7, 42.7, 34.5, 30.3, 27.9, 21.1.

6G-4

^{1}H NMR (400 MHz, TFA-*d*) δ 4.83 (s, 4H), 3.40 (s, 4H), 2.57 (s, 4H), 1.74 (s, 4H), 1.60 (s, 4H), 1.37 (s, 4H). ^{13}C NMR (100 MHz, TFA-*d*) δ 178.2, 173.2, 64.7, 42.7, 35.1, 30.3, 28.0, 25.6.

6G-5

^{1}H NMR (400 MHz, TFA-*d*) δ 4.83 (s, 4H), 3.39 (t, *J* = 7.5 Hz, 4H), 2.53 (t, *J* = 7.7 Hz, 4H), 1.70 (p, *J* = 7.6 Hz, 4H), 1.58 (s, *J* = 7.6 Hz, 4H), 1.44 – 1.36 (m, 6H). ^{13}C NMR (100 MHz, TFA-*d*) δ 178.8, 173.2, 64.8, 42.7, 35.4, 30.3, 30.0, 27.9, 25.9.

6G-6

^{1}H NMR (400 MHz, TFA-*d*) δ 4.82 (d, *J* = 2.9 Hz, 4H), 3.38 (t, *J* = 7.0 Hz, 4H), 2.52 (t, *J* = 7.4 Hz, 4H), 1.68 (d, *J* = 8.9 Hz, 4H), 1.59 (s, 4H), 1.37 (s, 8H). ^{13}C NMR (100 MHz, TFA-*d*) δ 179.1, 173.3, 64.7, 42.7, 35.6, 30.3, 30.3, 27.9, 26.2.

6G-8

^{1}H NMR (400 MHz, TFA-*d*) δ 4.83 (s, 4H), 3.40 (t, *J* = 7.4 Hz, 4H), 2.52 (t, *J* = 7.6 Hz, 4H), 1.67 (s, 4H), 1.59 (s, 4H), 1.37 (s, 4H), 1.32 (s, 6H). ^{13}C NMR (100 MHz, TFA-*d*) δ 179.5, 173.3, 64.7, 42.6, 35.8, 30.7, 30.7, 30.3, 27.9, 26.5.

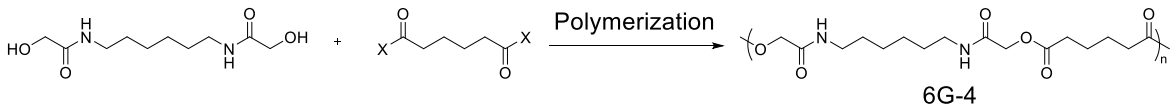
2G-4

^{1}H NMR (400 MHz, TFA-*d*) δ 4.91 (s, 4H), 3.73 (s, 4H), 2.68 (s, 4H), 1.84 (s, 4H). ^{13}C NMR (100 MHz, TFA-*d*) δ 178.2, 174.0, 64.9, 41.3, 35.2, 25.6.

4G-4

^{1}H NMR (400 MHz, TFA-*d*) δ 4.92 (s, 4H), 3.53 (s, 4H), 2.66 (s, 4H), 1.83 (s, 4H), 1.75 (s, 4H). ^{13}C NMR (100 MHz, TFA-*d*) δ 178.3, 173.3, 64.8, 42.0, 35.2, 27.7, 25.6.

Table S1. Synthesis of 6G-4



Entry	X	Reagents	Solvent	Temp (°C)	Time (h)	M_n[a] (kg/mol)	$Đ$[a]	Yield[b] (%)
1	OMe	$Ti(OiPr)_4$	Neat	180	7	-	-	<5%
2	OMe	$Sn(Oct)_2$	Neat	180	7	-	-	<5%
3	OMe	Li(acac)	Neat	180	7	-	-	<5%
4	OMe	$Zn(OAc)_2 \cdot 2H_2O$	Neat	180	7	-	-	<5%
5	OMe	TsOH	Neat	180	7	-	-	<5%
6	OMe	TBD	Neat	180	7	-	-	<5%
7	Cl	-	Toluene	95 → 110	8	7.8	2.7	50
8	OH	EDC·HCl, DMAP	DCM	r.t.	24	14	1.9	79

[a]Determined by HFIP SEC (0.025 M KTFA) at 40 °C calibrated by using PMMA standards. [b]Obtained after purification from methanol.

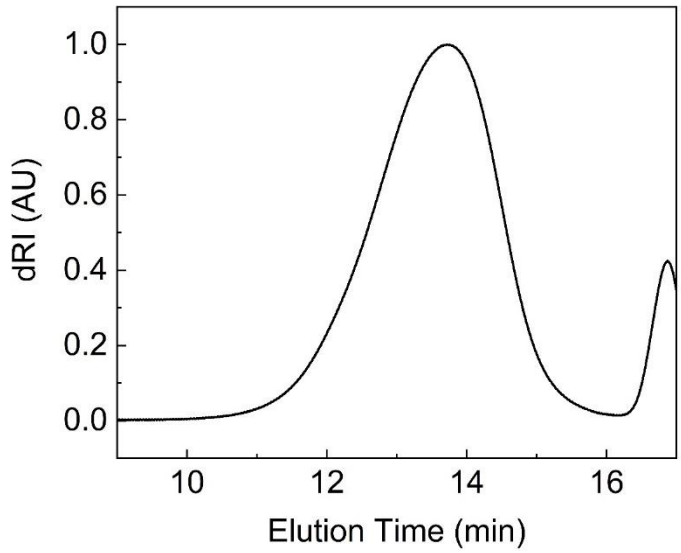


Figure S1. SEC trace of 6G-4 synthesized from adipoyl chloride and 6G. HFIP SEC (0.025 M KTFA) at 40 °C calibrated by using PMMA standards.

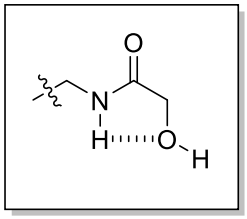


Figure S2. Possible intramolecular hydrogen bonding between amide and alcohol in diamidodiols

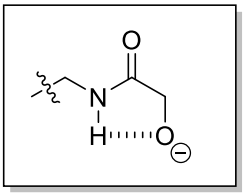
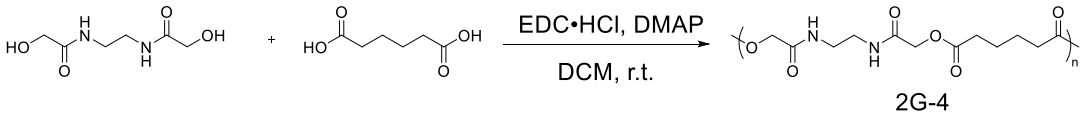


Figure S3. Possible intramolecular hydrogen bonding between amide and alkoxide in deprotonated diamidodiols

Table S2. Synthesis of Different Molar Mass 2G-4



2G-4

Entry	Time (h)	M_n[a] (kg/mol)	M_w[a] (kg/mol)	$Đ$[a]	Yield[b] (%)
1	4.5	12	23	1.9	59
2	8	15	27	1.8	52
3	14	17	34	2.0	74
4	24	31	62	2.0	67

[a]Determined by HFIP SEC (0.025 M KTFA) at 40 °C calibrated by using PMMA standards. [b]Obtained after purification from methanol.

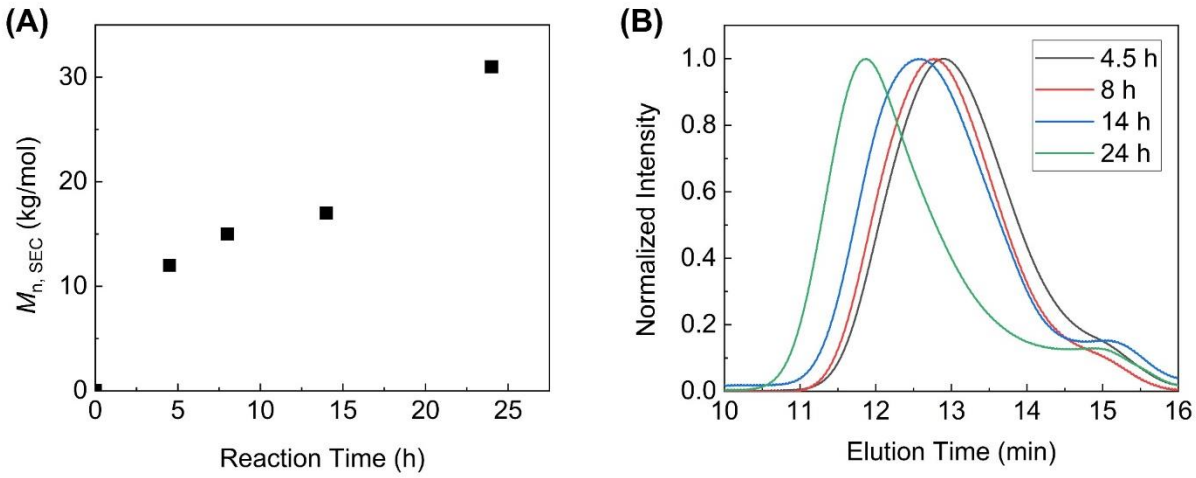
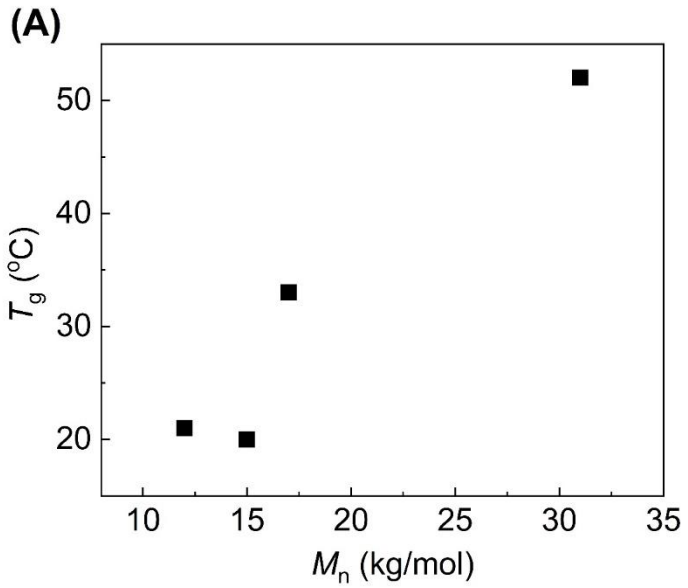


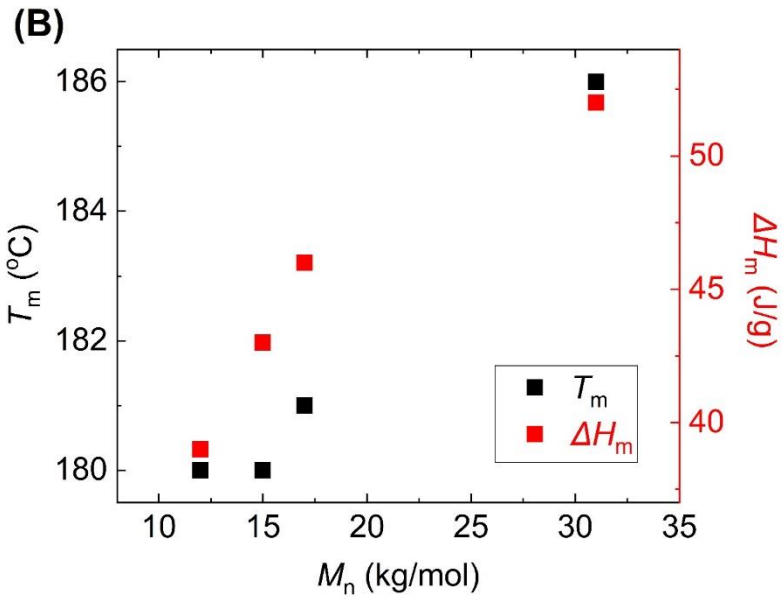
Figure S4. (A) $M_{n, SEC}$ vs reaction time. (B) SEC traces of different molar mass 2G-4. Molar mass data were determined by HFIP SEC (0.025 M) at 40 °C calibrated by using PMMA standards.

Table S3. Summary of Thermal Properties of Different Molar Mass 2G-4

Polymer	M_n[a] **(kg/mol)**	T_g[b] (°C)	T_m[b] (°C)	ΔH_m[b] **(J/g)**	T_c[c] (°C)	ΔH_c[c] **(J/g)**
2G-4	12	21	180	39	56	36
	15	20	180	43	64	51
	17	33	181	46	67	47
	31	52	186	52	128	54

[a]Determined by HFIP SEC (0.025 M) at 40 °C calibrated by using PMMA standards. [b]Determined by DSC analysis of powders under N_2 atmosphere starting from -20 °C at a heating rate of 10 °C/min based on the first heating cycle. [c]Determined by DSC analysis under N_2 atmosphere starting from -20 °C at a heating and cooling rate of 10 °C/min based on the first cooling cycle.


(A)
50
40
30
20
T_g (°C)
10
15
20
25
30
35
M_n (kg/mol)


(B)
186
184
182
180
T_m (°C)
50
45
40
ΔH_m (J/g)
T_m
ΔH_m
10
15
20
25
30
35
M_n (kg/mol)

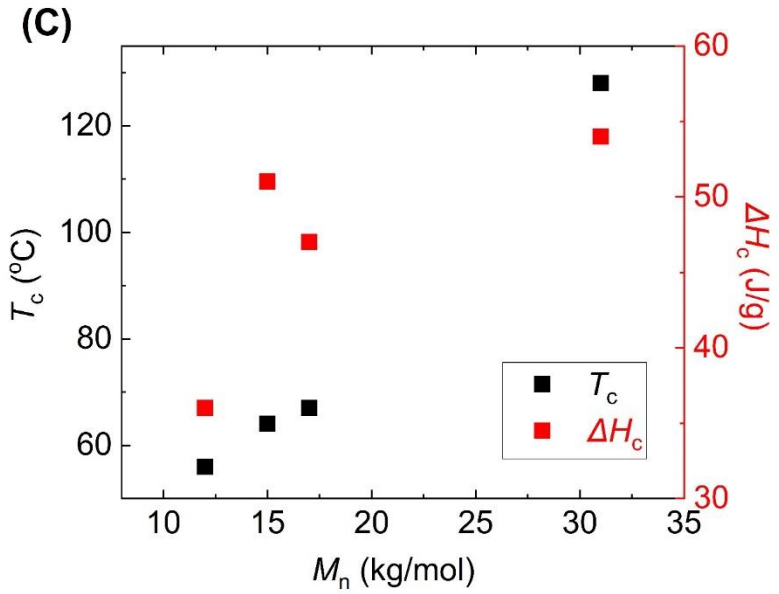


Figure S5. Effect of molar mass of 2G-4 on (A) glass transition temperature (T_g) in the first heating cycle starting from -20 °C at a heating rate of 10 °C/min, (B) melting temperature (T_m) and enthalpy of melting (ΔH_m) in the first heating cycle starting from -20 °C at a heating rate of 10 °C/min, and (C) crystallization temperature (T_c) and enthalpy of crystallization (ΔH_c) in the first cooling cycle starting from -20 °C at a heating and cooling rate of 10 °C/min.

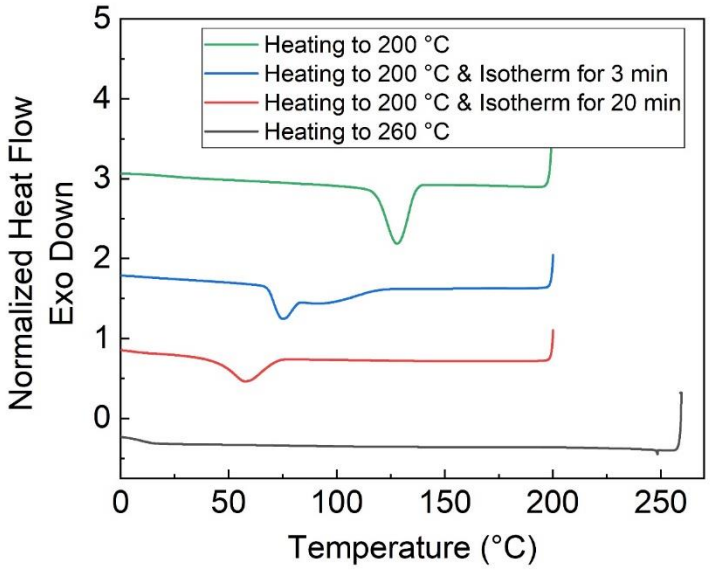


Figure S6. Effect of isotherm experiments at 200 °C on crystallization temperature starting from -20 °C at a heating and cooling rate of 10 °C/min.

Table S4. Summary of Mechanical Properties of Poly(ester-amide)s

Polymer	$M_{n,\,SEC}$ (kg/mol)	Elastic modulus, E^a (GPa)	Yield strength, $\sigma_y{}^a$ (MPa)	Ultimate strength, $\sigma_b{}^a$ (MPa)	Elongation at break, $\varepsilon_b{}^a$ (%)	Toughness[a] (MJ m^{-3})
6G-2	15	1.1 ± 0.4	ND[b]	11 ± 4	1.4 ± 0.6	0.11 ± 0.08
6G-3	19	0.37 ± 0.05	14 ± 2	12 ± 5	130 ± 60	17 ± 7
6G-4	14	0.41 ± 0.16	12 ± 2	10 ± 2	39 ± 15	4 ± 2
6G-5	17	0.25 ± 0.05	ND[b]	10 ± 1	15 ± 1	1.4 ± 0.3
6G-5	27	0.24 ± 0.03	11 ± 2	24 ± 3	342 ± 40	59 ± 11
6G-6	16	0.39 ± 0.09	13 ± 2	10 ± 4	100 ± 40	13 ± 6
6G-8	10	0.7 ± 0.2	ND[b]	8 ± 2	2.1 ± 0.9	0.12 ± 0.08
6G-8	32	0.53 ± 0.10	15 ± 2	21 ± 5	310 ± 70	60 ± 20
2G-4	17	-[c]	-[c]	-[c]	-[c]	-[c]
2G-4	36	0.9 ± 0.2	19 ± 2	18 ± 4	133 ± 40	25 ± 8
4G-4	11	0.29 ± 0.04	ND[b]	4 ± 3	2.7 ± 1.5	0.12 ± 0.09

[a]Average values and standard deviations are reported for tensile tests of at least 5 samples extended at 1 mm min^{-1}; toughness was calculated as area under the stress–strain curve. [b]Yield point was not detected. [c]It was too brittle to make the film.

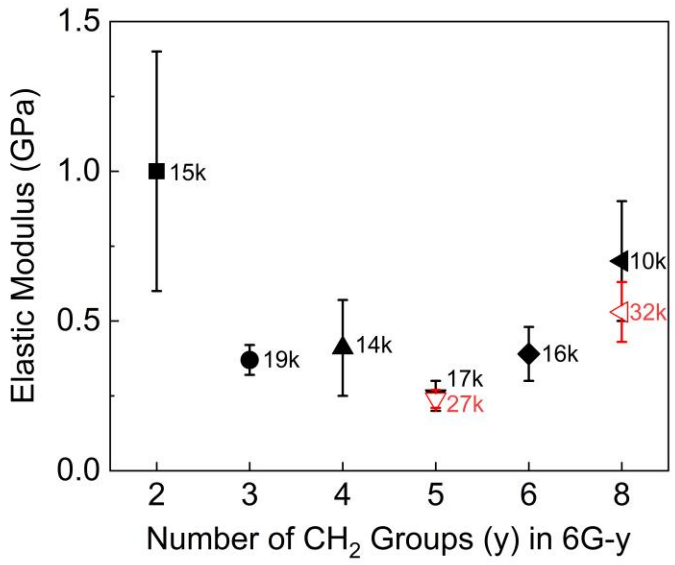


Figure S7. The effect of methylene groups of 6G-y on elastic modulus. The extension rate was 1 mm min^{-1}.

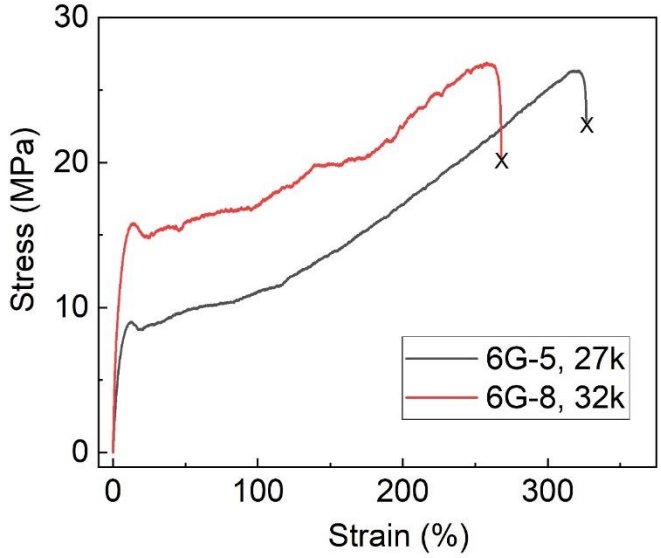


Figure S8. Representative stress-strain curve of 6G-5 (27 kg/mol) and 6G-8 (32 kg/mol). The extension rate was 1 mm min^{-1} up to its break point indicated by X.

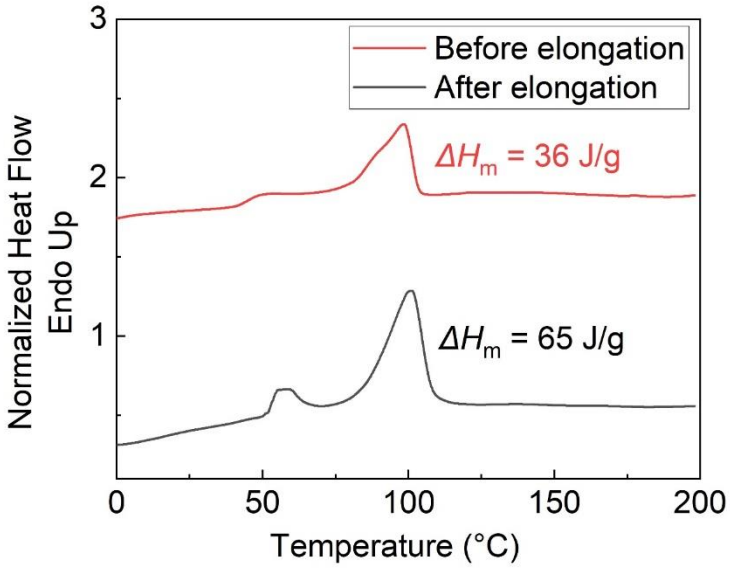


Figure S9. 1st heating cycle of 6G-5 before and after elongation (extension rate of 1 mm min^{-1}) with the heating rate of 10 °C/min.

Table S5. Summary of oxygen and water vapor permeability of poly(ester-amide)s

Polymer	Oxygen permeability[a] ($cc.mil.m^{-2}d^{-1}.atm^{-1}$)	Water vapor permeability[b] ($g.mil.m^{-2}d^{-1}.kPa^{-1}$)
6G-4	48, 43	31 ± 3
6G-5	276, 244	30 ± 5
6G-6	93, 92	29 ± 7
6G-8	272, 200, 176, 138	41 ± 32

[a]Oxygen permeability of at least 2 samples at 23 °C, 0% relative humidity, 5 – 10 cm^2 of test area (masked) according to ASTM D3985-02 standard. [b]Average values and standard deviations are reported for water vapor permeabilities of 5 samples measured at around 19 °C and 51% relative humidity, 15 cm^2 of test area according to ASTM E96 standard.

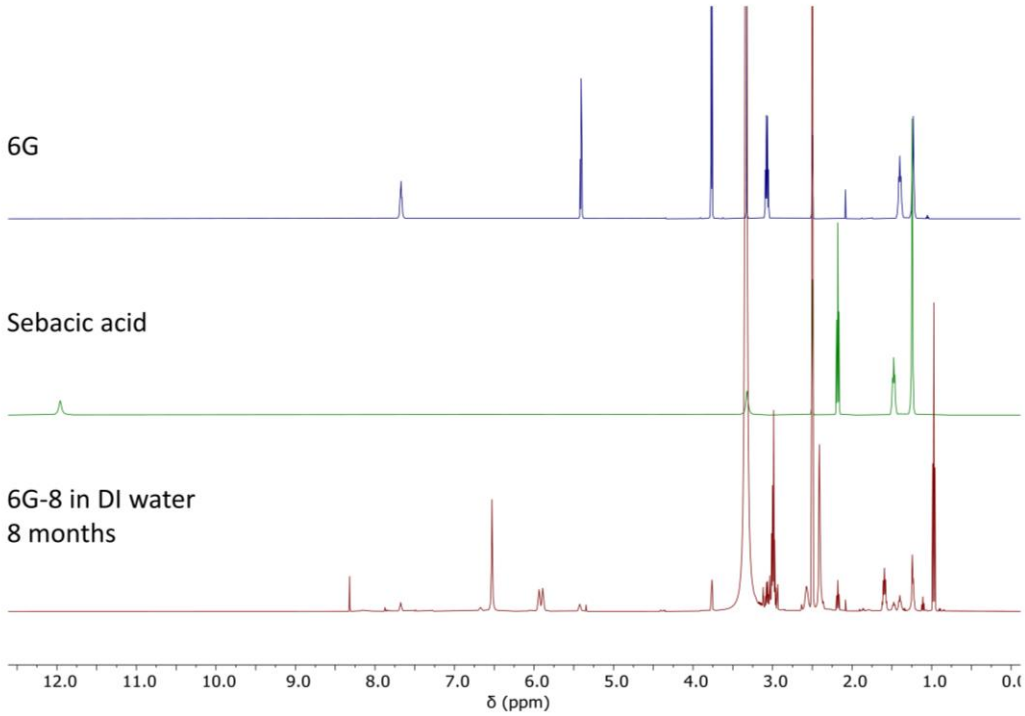


Figure S10. ^{1}H NMR analysis (DMSO-*d*) of hydrolyzed products from 6G-8 in DI water

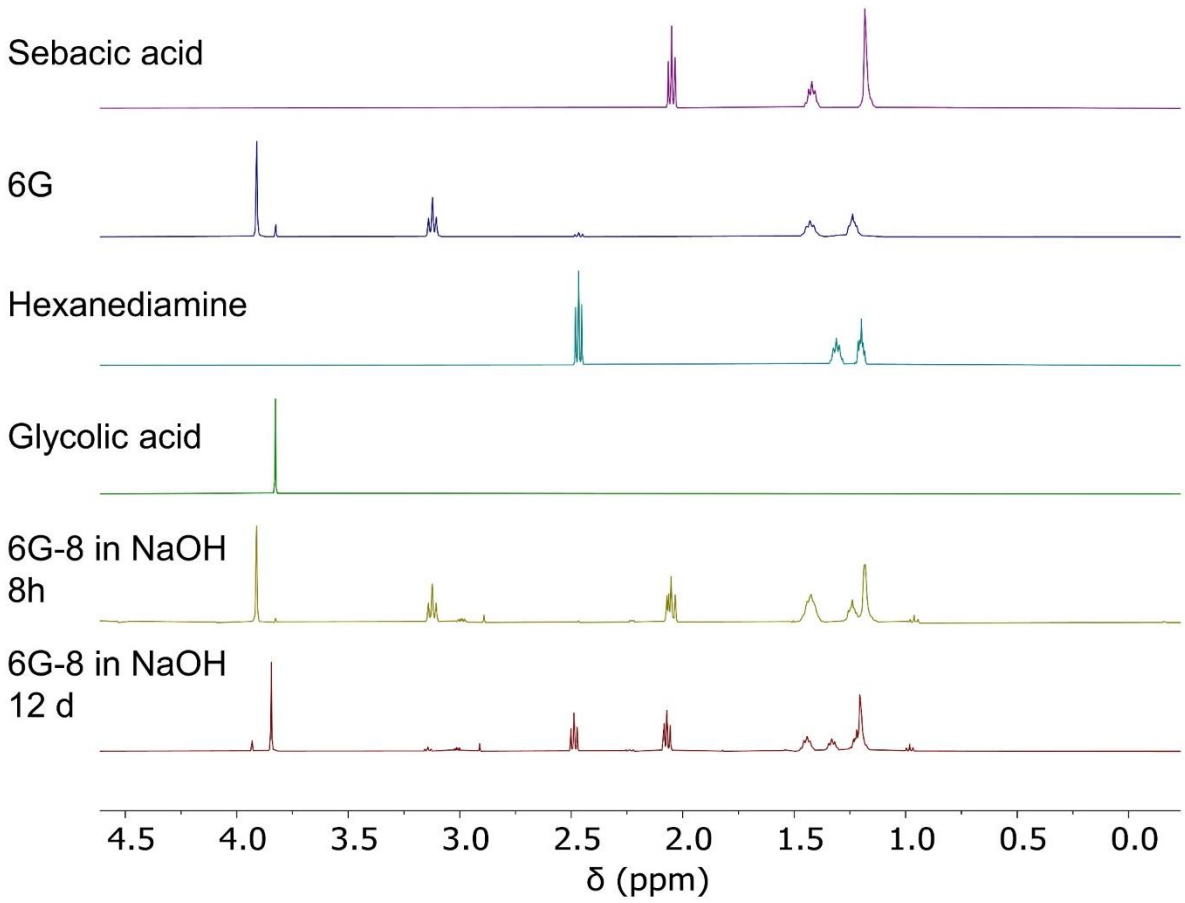


Figure S11. ^{1}H NMR analysis (1 M NaOH in D_2O) of hydrolyzed products from 6G-8

References

(1) Vera, M.; Admetlla, M.; Rodríguez-Galán, A.; Puiggalí, J. Synthesis, Characterization and Degradation Studies on the Series of Sequential Poly(Ester Amide)s Derived from Glycolic Acid, 1,6-Hexanediamine and Aliphatic Dicarboxylic Acids. *Polym. Degrad. Stab.* **2005**, *89* (1), 21–32.

NMR Spectra:

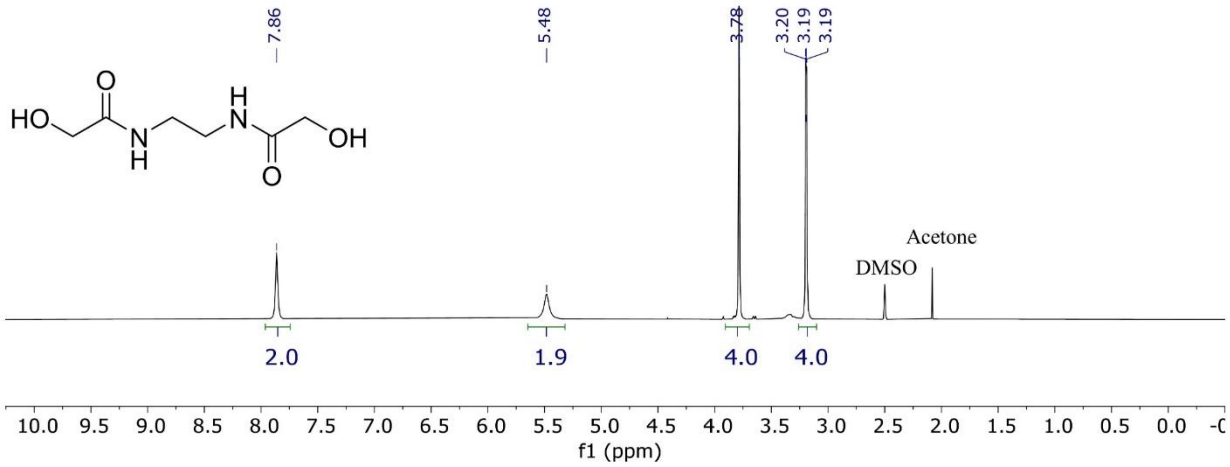


Figure S12. ^{1}H NMR spectra (500 MHz, DMSO-*d*) of 2G

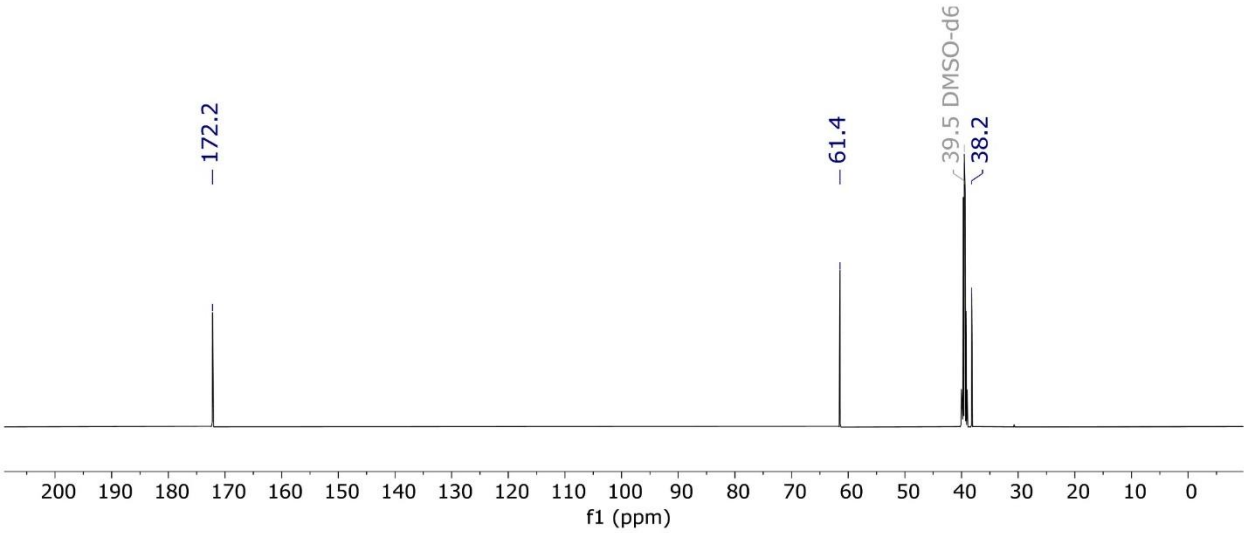


Figure S13. ^{13}C NMR spectra (125 MHz, DMSO-*d*) of 2G

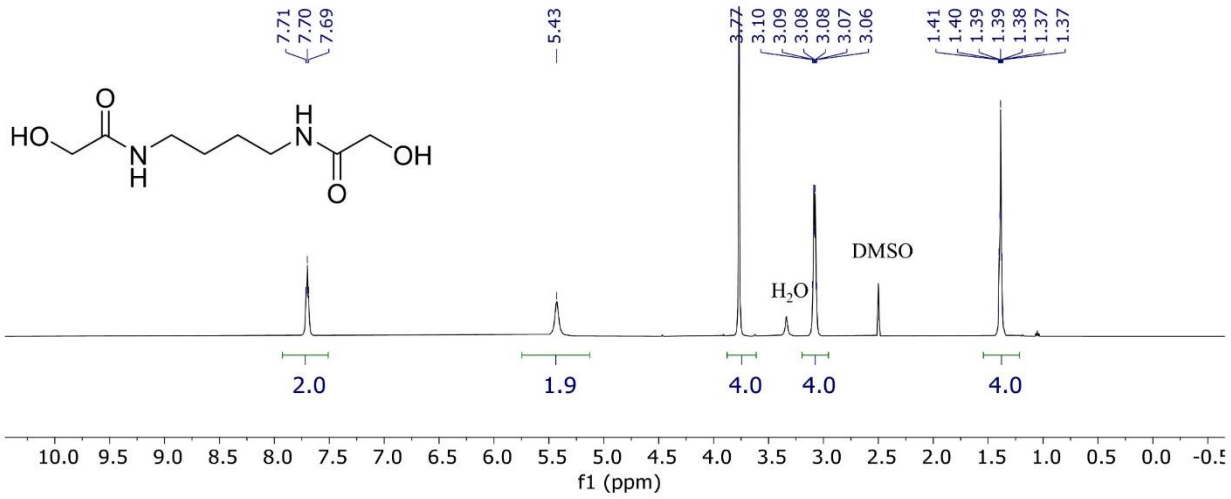


Figure S14. [1]H NMR spectra (500 MHz, DMSO-*d*) of 4G

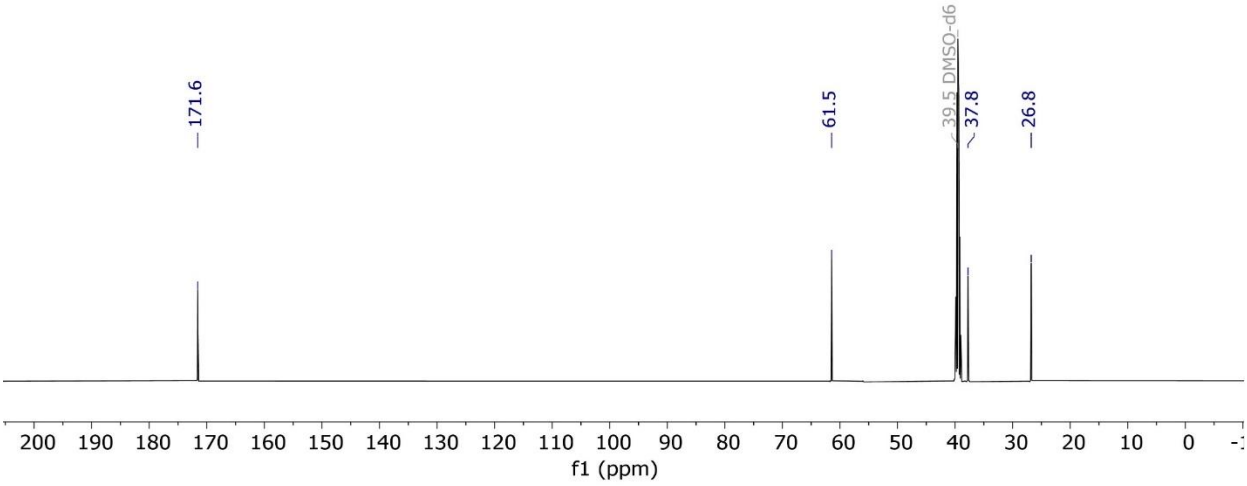


Figure S15. [13]C NMR spectra (125 MHz, DMSO-*d*) of 4G

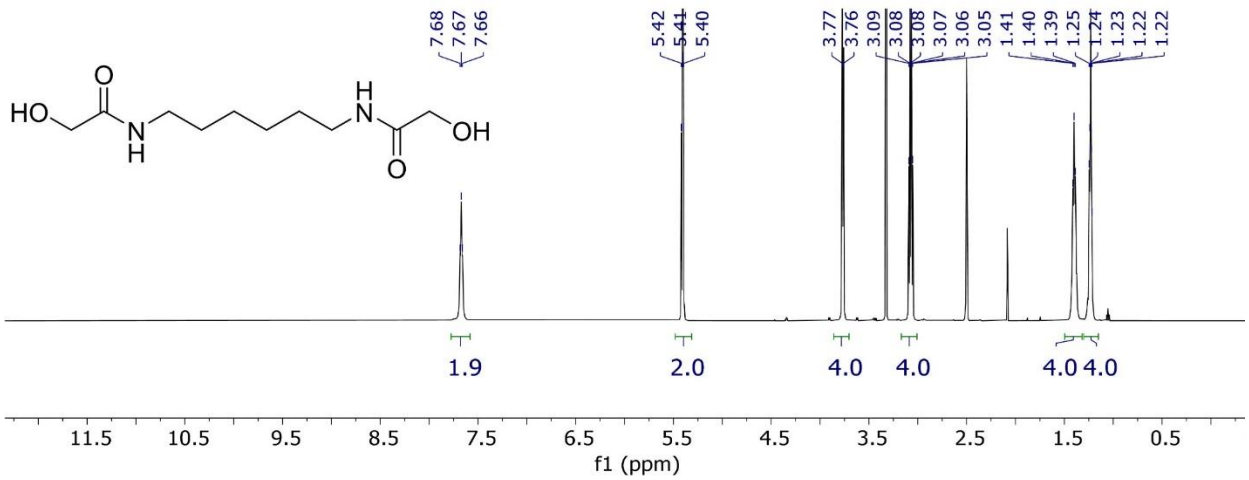


Figure S16. ^{1}H NMR spectra (500 MHz, DMSO-*d*) of 6G

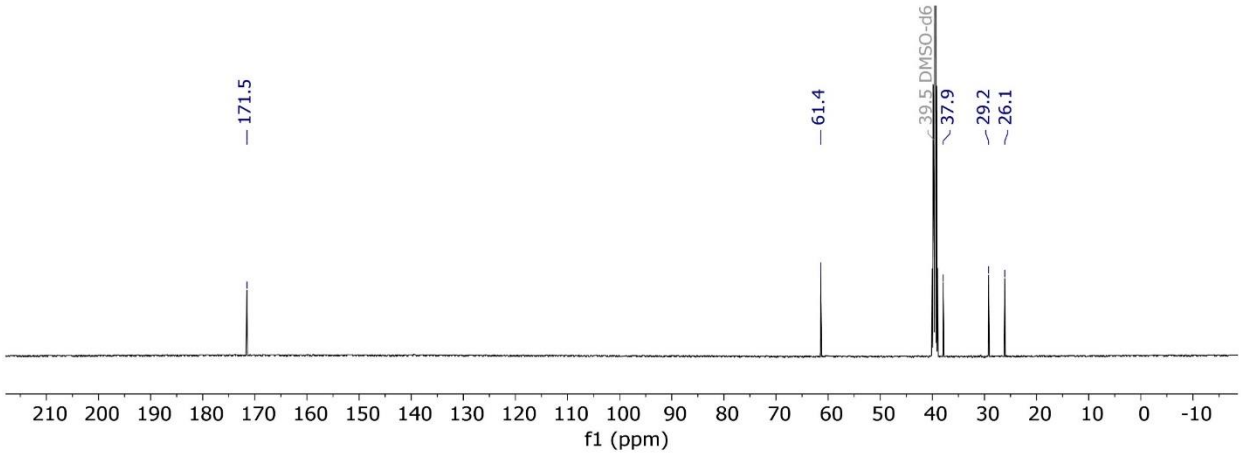


Figure S17. ^{13}C NMR spectra (125 MHz, DMSO-*d*) of 6G

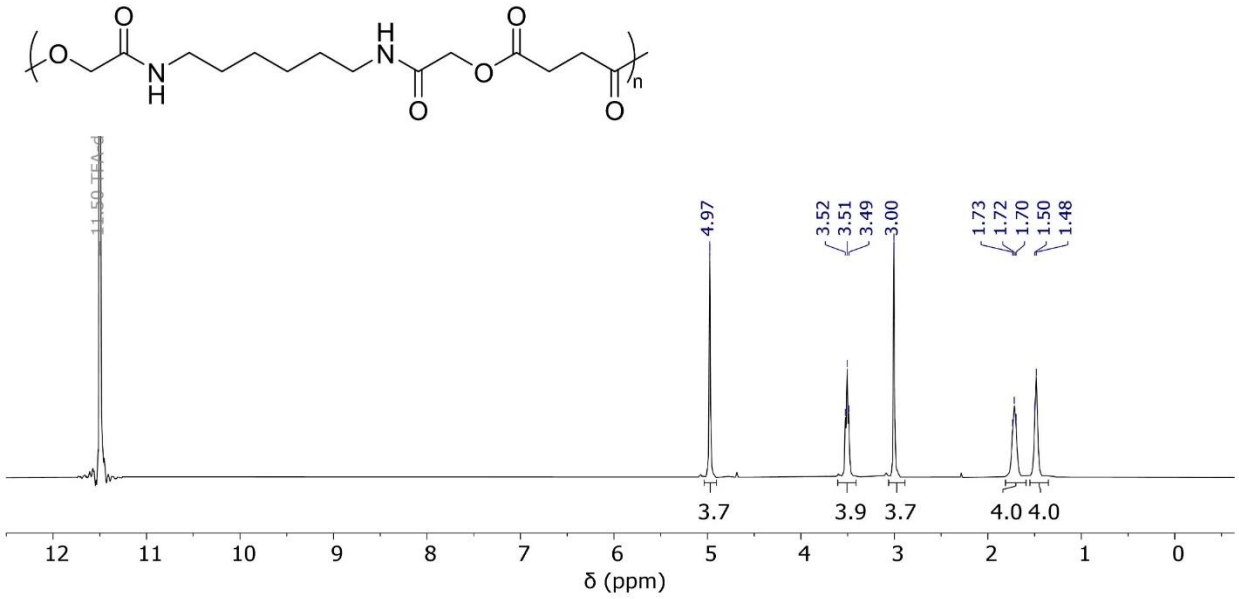


Figure S18. ^{1}H NMR spectra (400 MHz, TFA-*d*) of 6G-2

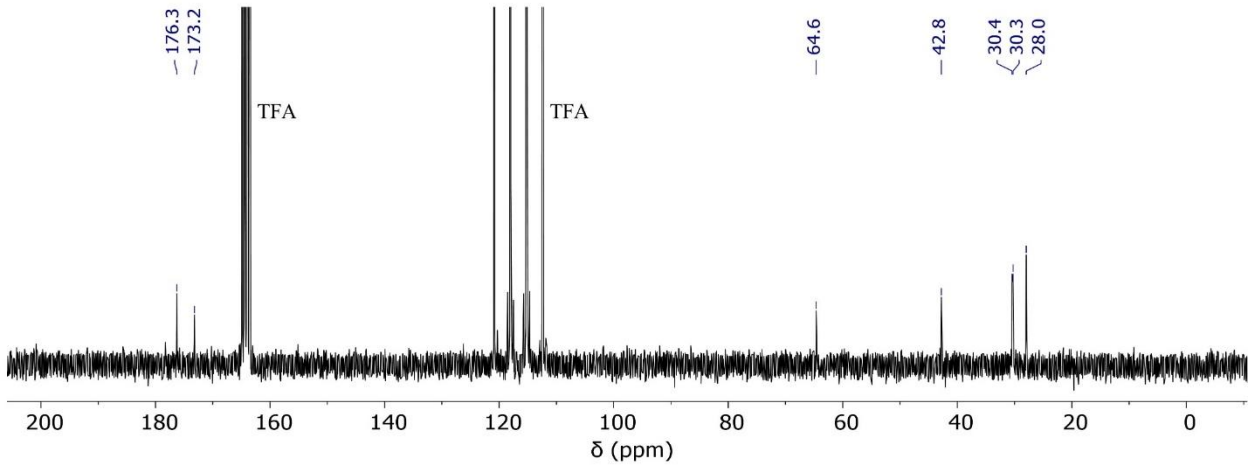


Figure S19. ^{13}C NMR spectra (100 MHz, TFA-*d*) of 6G-2

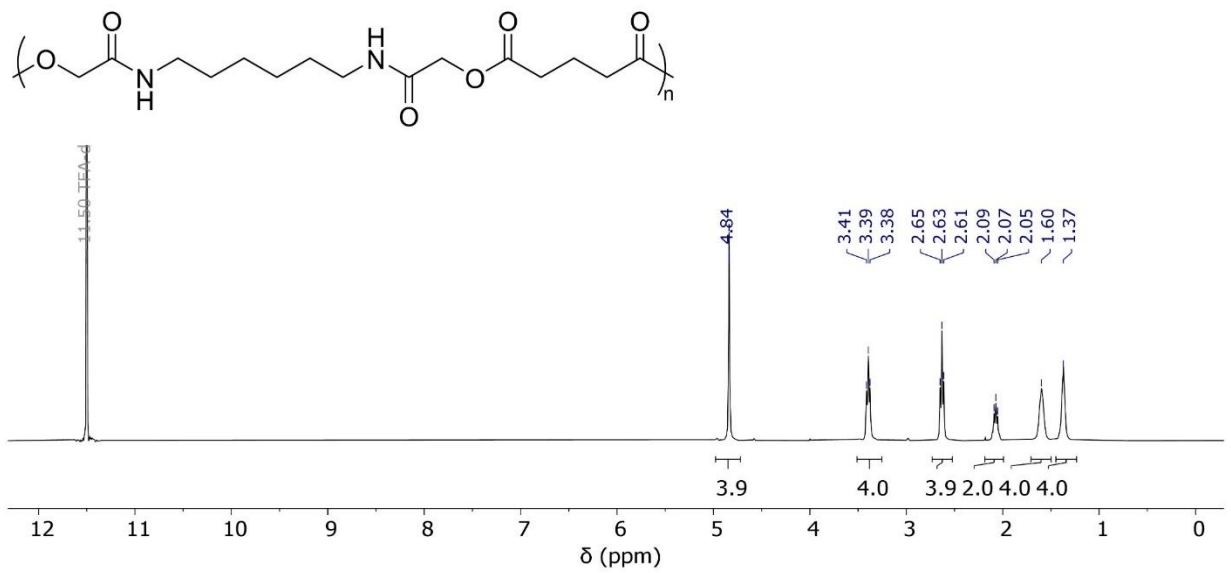


Figure S20. ^{1}H NMR spectra (400 MHz, TFA-*d*) of 6G-3

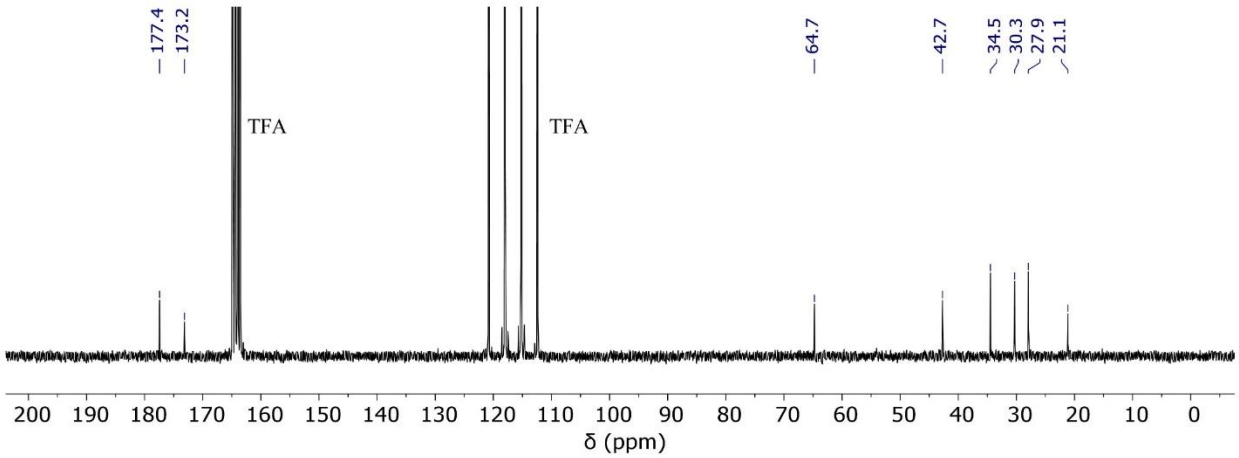


Figure S21. ^{13}C NMR spectra (100 MHz, TFA-*d*) of 6G-3

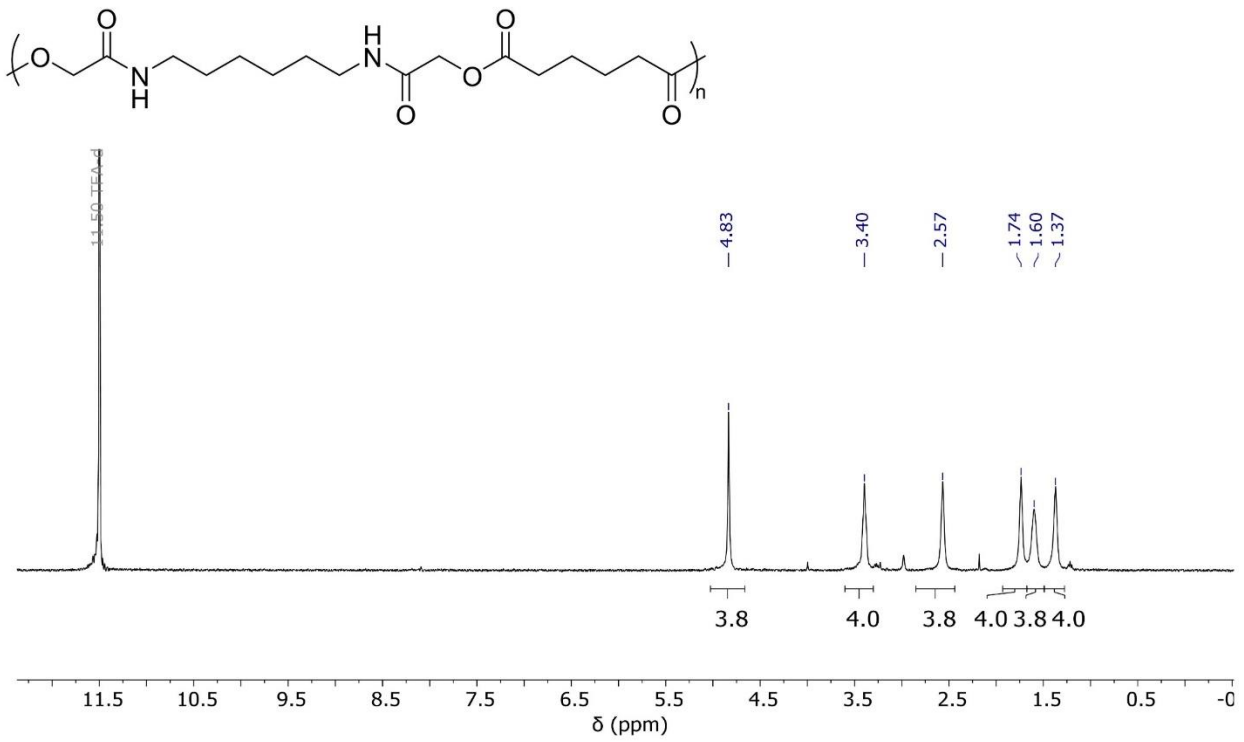


Figure S22. ^{1}H NMR spectra (400 MHz, TFA-*d*) of 6G-4

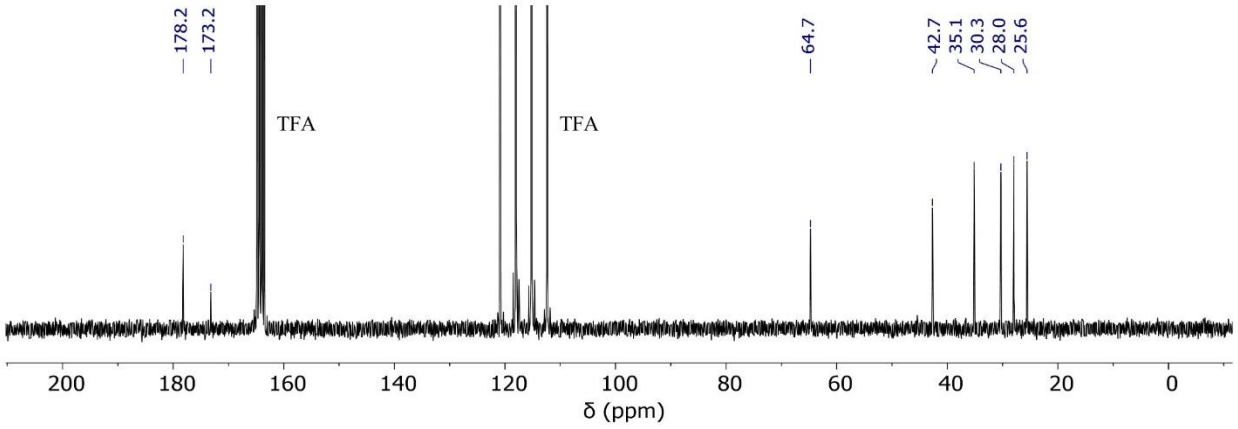


Figure S23. ^{13}C NMR spectra (100 MHz, TFA-*d*) of 6G-4

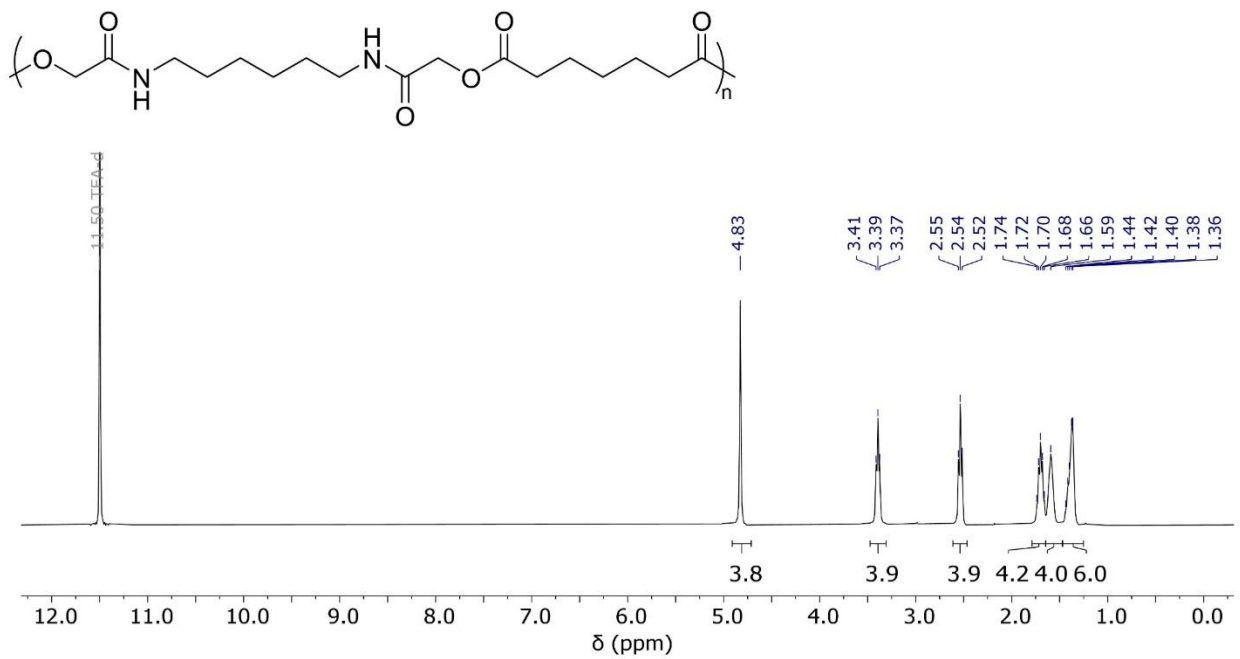


Figure S24. ^{1}H NMR spectra (400 MHz, TFA-*d*) of 6G-5

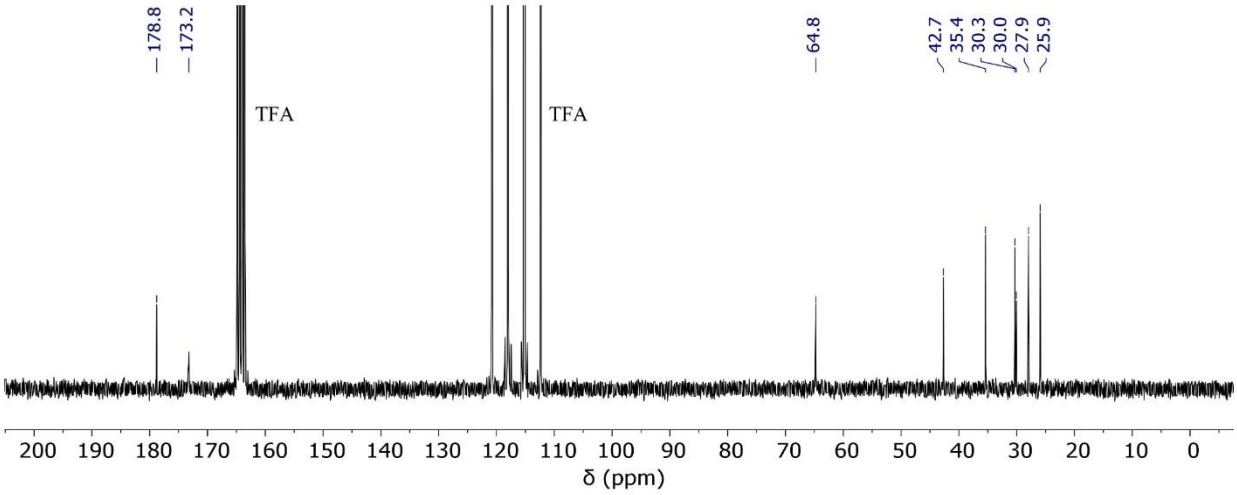


Figure S25. ^{13}C NMR spectra (100 MHz, TFA-*d*) of 6G-5

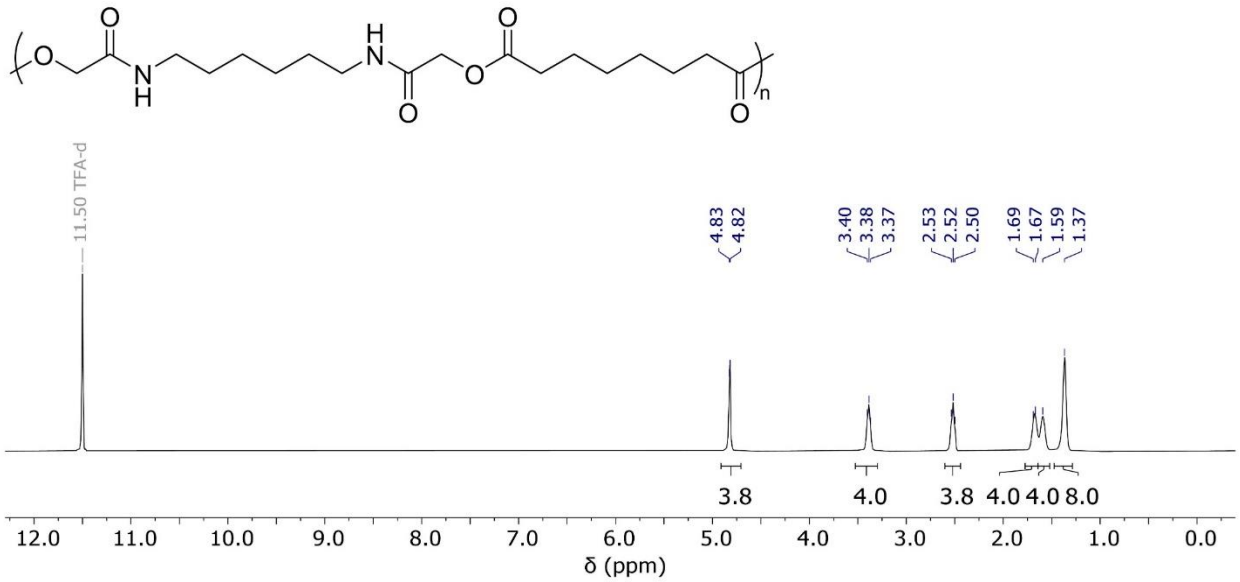


Figure S26. ^{1}H NMR spectra (400 MHz, TFA-*d*) of 6G-6

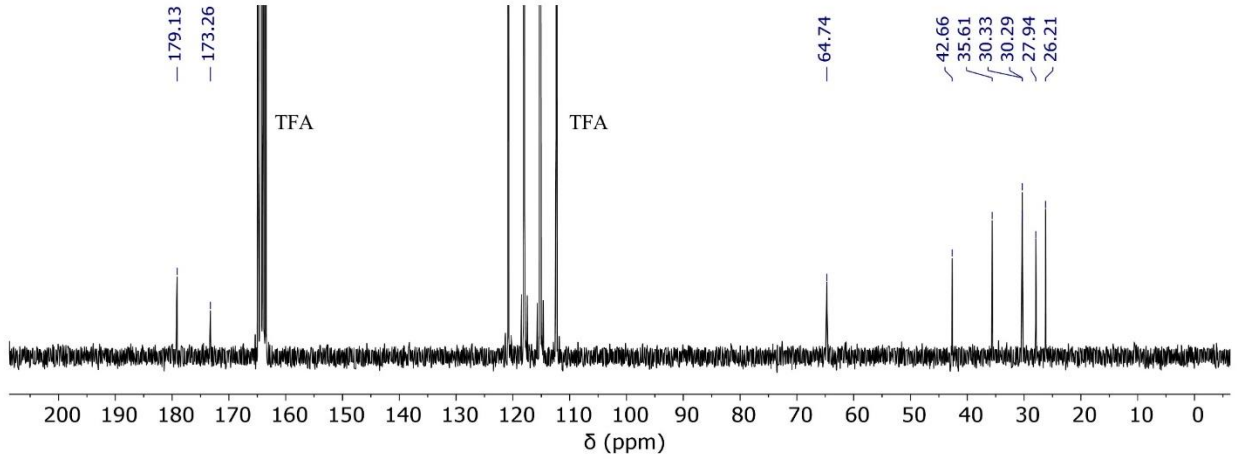


Figure S27. ^{13}C NMR spectra (100 MHz, TFA-*d*) of 6G-6

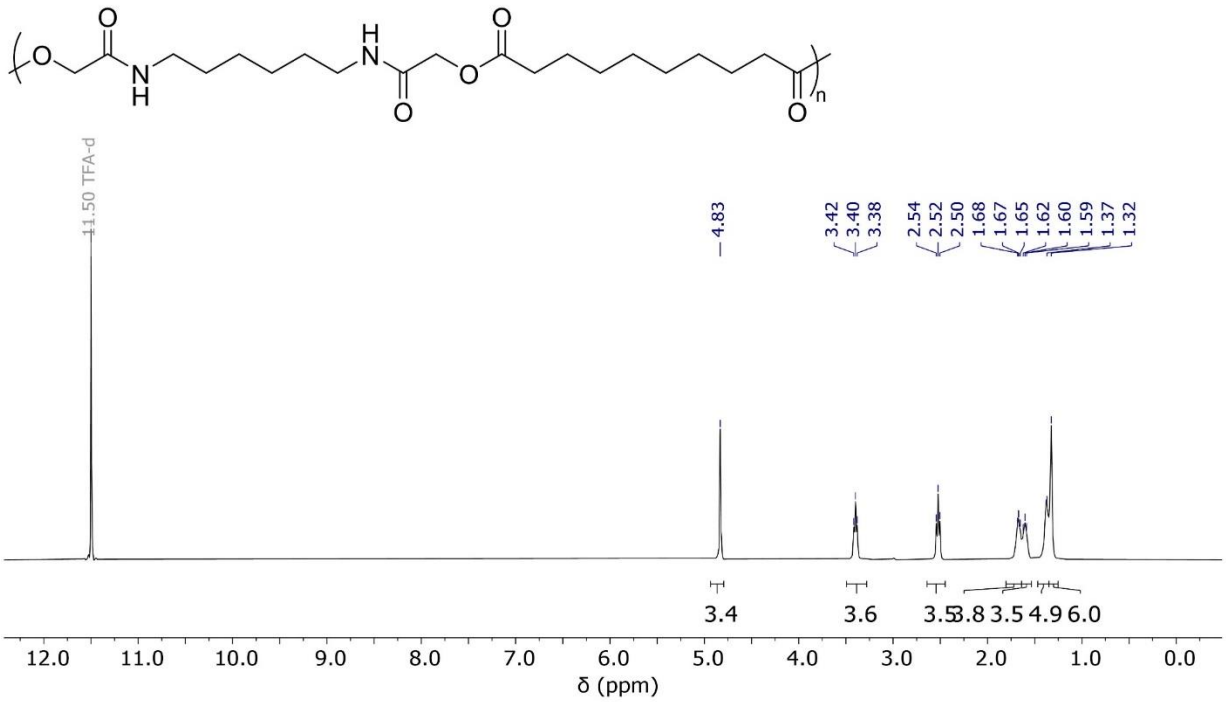


Figure S28. ^{1}H NMR spectra (400 MHz, TFA-*d*) of 6G-8

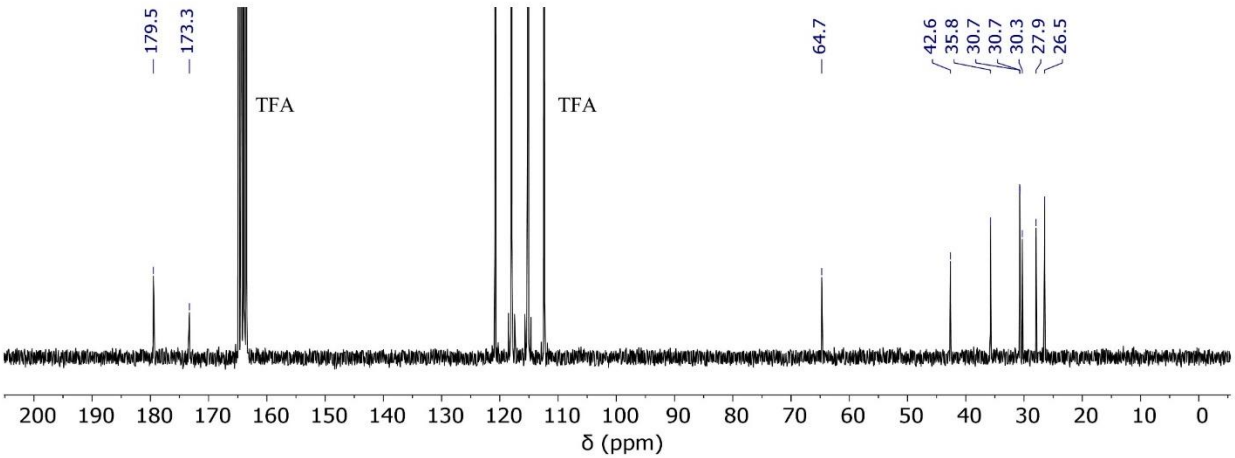


Figure S29. ^{13}C NMR spectra (100 MHz, TFA-*d*) of 6G-8

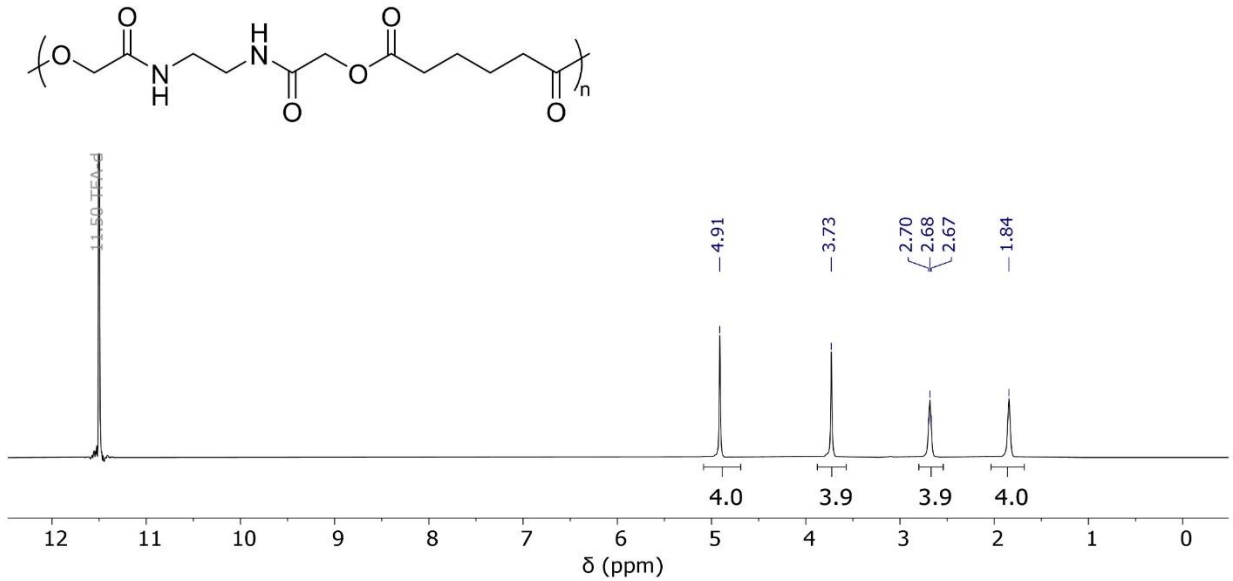


Figure S30. ^{1}H NMR spectra (400 MHz, TFA-*d*) of 2G-4

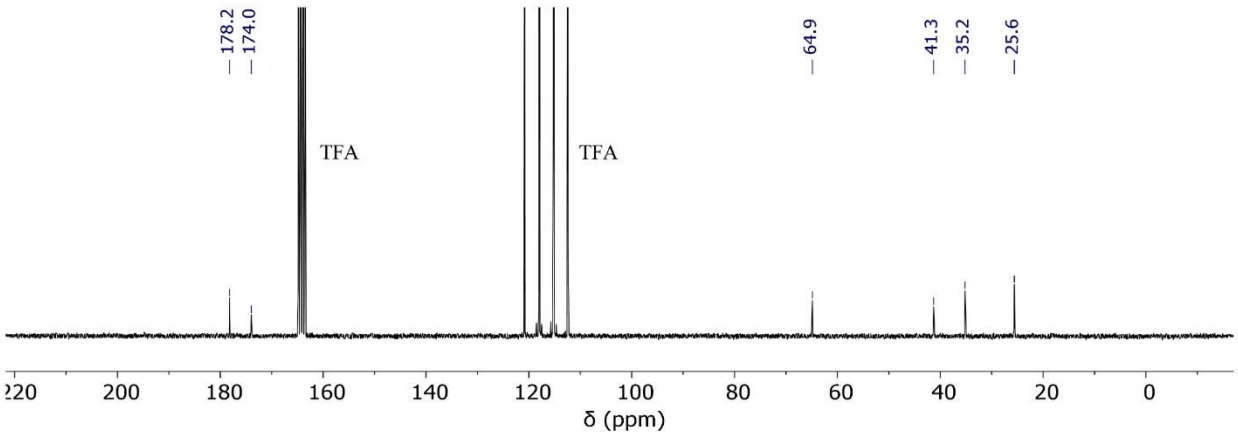


Figure S31. ^{13}C NMR spectra (100 MHz, TFA-*d*) of 2G-4

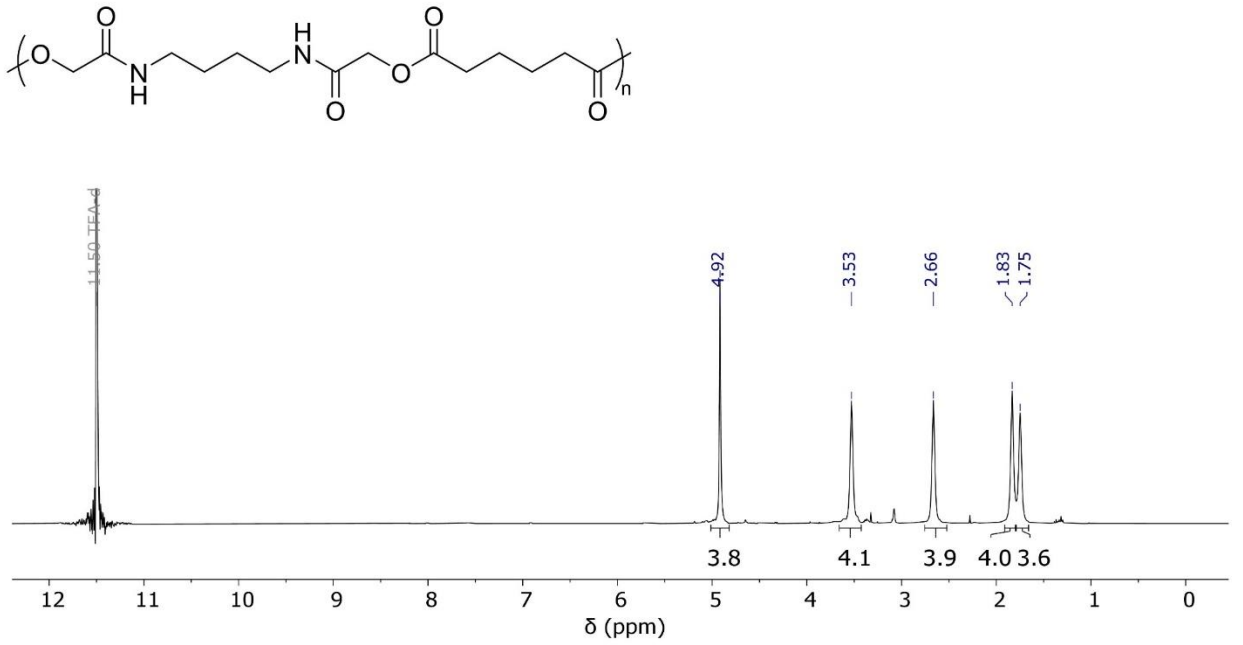


Figure S32. ^{1}H NMR spectra (400 MHz, TFA-*d*) of 4G-4

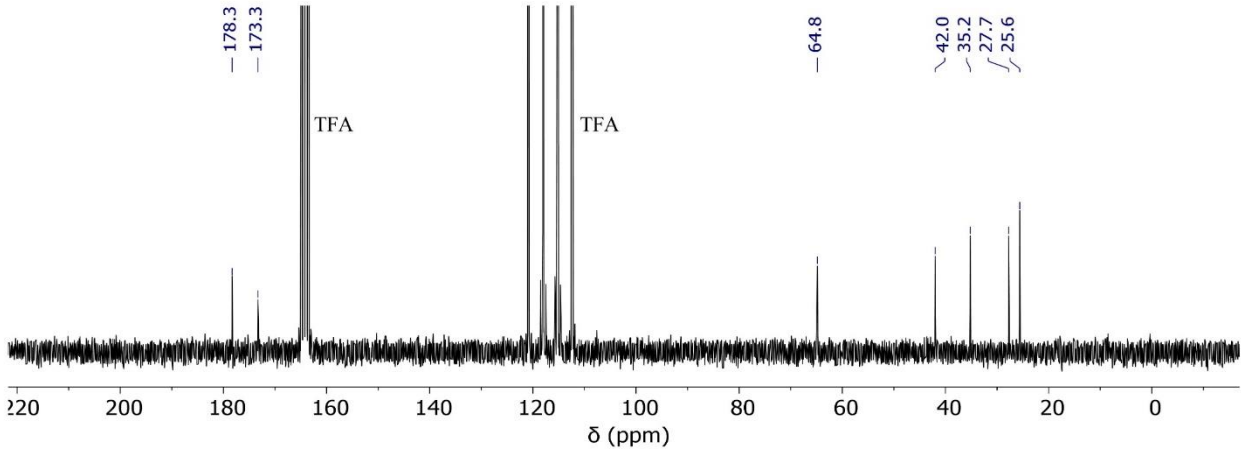


Figure S33. ^{13}C NMR spectra (100 MHz, TFA-*d*) of 2G-4

X-ray crystallography data:

2G

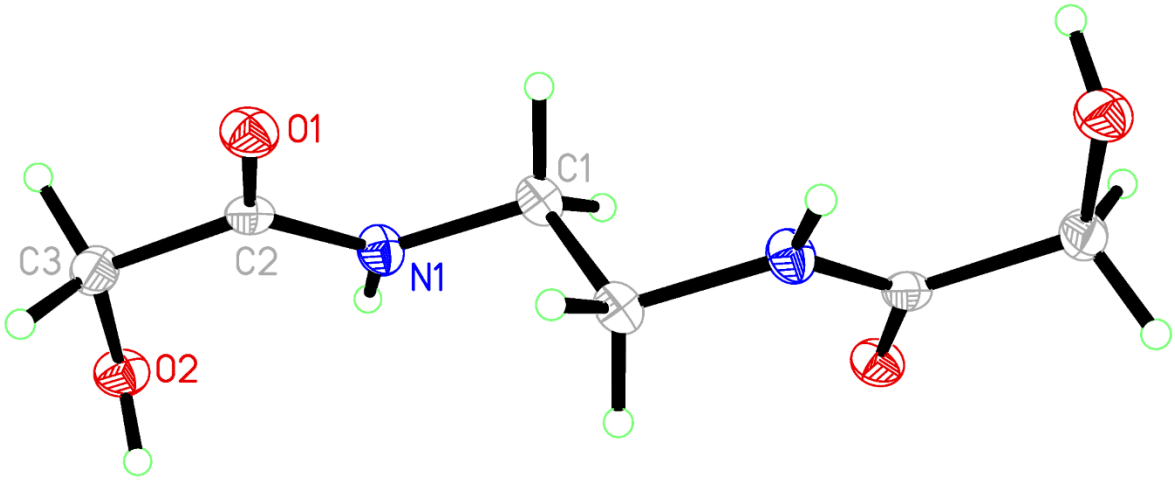


Table S6. Crystal data and structure refinement for 2G

Empirical formula	$C_6H_{12}N_2O_4$	
Formula weight	176.18	
Temperature	125(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 20.8643(19) Å	α = 90°
	b = 4.5307(4) Å	β = 102.292(4)°
	c = 8.7480(7) Å	γ = 90°
Volume	807.99(12) $Å^3$	
Z	4	
Density (calculated)	1.448 Mg/m^3	
Absorption coefficient	0.122 mm^{-1}	
F(000)	376	
Crystal color, morphology	colorless, plate	
Crystal size	0.230 x 0.130 x 0.025 mm^3	
Theta range for data collection	3.998 to 30.596°	
Index ranges	$-29 \le h \le 29$, $-6 \le k \le 6$, $-12 \le l \le 10$	
Reflections collected	4006	
Independent reflections	1241 [R(int) = 0.0368]	
Observed reflections	994	
Completeness to theta = 25.242°	99.5%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7461 and 0.6404	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1241 / 2 / 61	
Goodness-of-fit on F^2	1.093	
Final R indices [I>2sigma(I)]	$R1$ = 0.0392, $wR2$ = 0.1093	
R indices (all data)	$R1$ = 0.0496, $wR2$ = 0.1170	
Largest diff. peak and hole	0.442 and -0.247 $e.Å^{-3}$	

Table S7. Bond lengths [Å] and angles [°] for 2G

O1-C2	1.2468(12)
N1-C2	1.3294(14)
N1-C1	1.4550(14)
N1-H1A	0.907(3)
C1-C1#1	1.525(2)
C1-H1B	0.9900
C1-H1C	0.9900
O2-C3	1.4112(13)
O2-H2A	0.841(3)
C2-C3	1.5159(15)
C3-H3A	0.9900
C3-H3B	0.9900
C2-N1-C1	122.79(9)
C2-N1-H1A	118.6(9)
C1-N1-H1A	118.5(9)
N1-C1-C1#1	111.62(11)
N1-C1-H1B	109.3
C1#1-C1-H1B	109.3
N1-C1-H1C	109.3
C1#1-C1-H1C	109.3
H1B-C1-H1C	108.0
C3-O2-H2A	107.1(10)
O1-C2-N1	123.33(10)
O1-C2-C3	120.60(10)
N1-C2-C3	116.06(9)
O2-C3-C2	113.71(9)
O2-C3-H3A	108.8
C2-C3-H3A	108.8
O2-C3-H3B	108.8
C2-C3-H3B	108.8
H3A-C3-H3B	107.7

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table S8. Torsion angles [°] for 2G

C2-N1-C1-C1#1	77.71(15)
C1-N1-C2-O1	-1.26(17)
C1-N1-C2-C3	177.66(9)
O1-C2-C3-O2	-168.58(10)
N1-C2-C3-O2	12.47(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Table S9. Hydrogen bonds for 2G [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1A...O1#2	0.907(3)	2.079(7)	2.9132(12)	152.4(12)
O2-H2A...O1#3	0.841(3)	1.904(3)	2.7445(12)	178.2(15)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 x,-y+1,z-1/2 #3 x,-y,z-1/2

4G

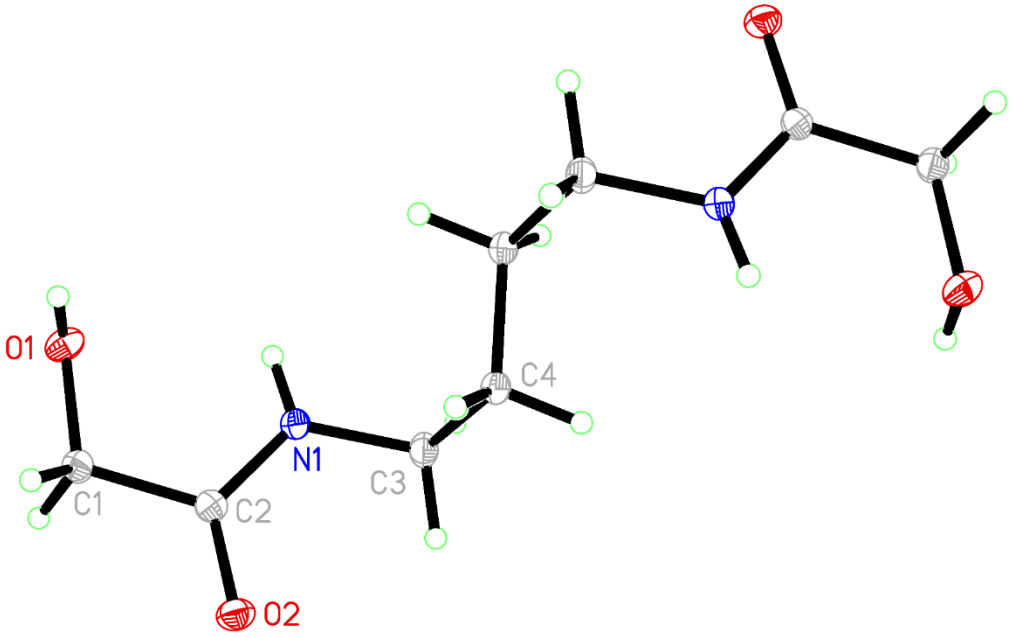


Table S10. Crystal data and structure refinement for 4G

Empirical formula	$C_8 H_{16} N_2 O_4$	
Formula weight	204.23	
Temperature	125(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.1288(6) Å	α = 90°
	b = 7.5360(6) Å	β = 113.285(2)°
	c = 8.5510(6) Å	γ = 90°
Volume	481.16(6) $Å^3$	
Z	2	
Density (calculated)	1.410 Mg/m^3	
Absorption coefficient	0.113 mm^{-1}	
F(000)	220	
Crystal color, morphology	Colourless, Block	
Crystal size	0.250 x 0.230 x 0.200 mm^3	
Theta range for data collection	2.728 to 30.494°	
Index ranges	$-11 \le h \le 11$, $-10 \le k \le 10$, $-12 \le l \le 12$	
Reflections collected	7826	
Independent reflections	1473 [R(int) = 0.0437]	
Observed reflections	1376	
Completeness to theta = 25.242°	100.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7461 and 0.6915	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1473 / 0 / 68	
Goodness-of-fit on F^2	1.072	
Final R indices [I>2sigma(I)]	$R1$ = 0.0347, $wR2$ = 0.0928	
R indices (all data)	$R1$ = 0.0367, $wR2$ = 0.0950	
Largest diff. peak and hole	0.333 and -0.297 $e.Å^{-3}$	

Table S11. Bond lengths [Å] and angles [°] for 4G

O1-C1	1.4103(10)	O2-C2	1.2467(9)
O1-H1A	0.8400	C3-C4	1.5242(11)
N1-C2	1.3315(10)	C3-H3A	0.9900
N1-C3	1.4652(10)	C3-H3B	0.9900
N1-H1B	0.840(13)	C4-C4#1	1.5234(15)
C1-C2	1.5169(11)	C4-H4A	0.9900
C1-H1C	0.9900	C4-H4B	0.9900
C1-H1D	0.9900		

C1-O1-H1A	109.5	N1-C3-C4	112.59(6)
C2-N1-C3	122.10(7)	N1-C3-H3A	109.1
C2-N1-H1B	118.6(9)	C4-C3-H3A	109.1
C3-N1-H1B	119.3(9)	N1-C3-H3B	109.1
O1-C1-C2	114.38(6)	C4-C3-H3B	109.1
O1-C1-H1C	108.7	H3A-C3-H3B	107.8
C2-C1-H1C	108.7	C3-C4-C4#1	113.28(8)
O1-C1-H1D	108.7	C3-C4-H4A	108.9
C2-C1-H1D	108.7	C4#1-C4-H4A	108.9
H1C-C1-H1D	107.6	C3-C4-H4B	108.9
O2-C2-N1	123.51(7)	C4#1-C4-H4B	108.9
O2-C2-C1	119.48(7)	H4A-C4-H4B	107.7
N1-C2-C1	117.02(7)		

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z+1

Table S12. Torsion angles [°] for 4G

C3-N1-C2-O2	-1.12(12)
C3-N1-C2-C1	178.54(7)
O1-C1-C2-O2	177.39(7)
O1-C1-C2-N1	-2.29(10)
C2-N1-C3-C4	-104.79(8)
N1-C3-C4-C4#1	-70.02(10)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z+1

Table S13. Hydrogen bonds for 4G [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1A...O2#2	0.84	1.90	2.7339(9)	170.2
N1-H1B...O2#3	0.840(13)	2.276(13)	3.0866(9)	162.4(12)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z+1 #2 -x+1,y-1/2,-z+3/2 #3 x,-y+1/2,z-1/2

6G

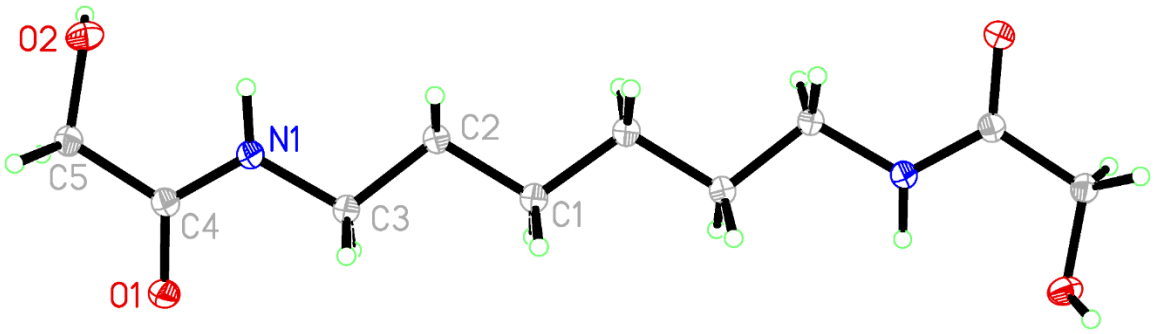


Table S14. Crystal data and structure refinement for 6G

Empirical formula	$C_{10}H_{20}N_2O_4$	
Formula weight	232.28	
Temperature	125(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 25.3633(17) Å	α = 90°
	b = 5.2161(3) Å	β = 103.025(3)°
	c = 8.9982(4) Å	γ = 90°
Volume	1159.81(12) $Å^3$	
Z	4	
Density (calculated)	1.330 Mg/m^3	
Absorption coefficient	0.102 mm^{-1}	
F(000)	504	
Crystal color, morphology	colourless, needle	
Crystal size	0.210 x 0.060 x 0.040 mm^3	
Theta range for data collection	3.298 to 30.757°	
Index ranges	$-36 \le h \le 30$, $-5 \le k \le 7$, $-12 \le l \le 12$	
Reflections collected	5679	
Independent reflections	1794 [R(int) = 0.0425]	
Observed reflections	1439	
Completeness to theta = 25.242°	99.8%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7461 and 0.6446	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1794 / 2 / 79	
Goodness-of-fit on F^2	1.088	
Final R indices [I>2sigma(I)]	$R1$ = 0.0429, $wR2$ = 0.1093	
R indices (all data)	$R1$ = 0.0551, $wR2$ = 0.1191	
Largest diff. peak and hole	0.319 and -0.363 $e.Å^{-3}$	

Table S15. Bond lengths [Å] and angles [°] for 6G

O1-C4	1.2493(12)	O2-H2A	0.863(16)
N1-C4	1.3322(13)	C2-C3	1.5173(14)
N1-C3	1.4582(13)	C2-H2B	0.9900
N1-H1A	0.909(2)	C2-H2C	0.9900
C1-C2	1.5221(15)	C3-H3A	0.9900
C1-C1#1	1.524(2)	C3-H3B	0.9900
C1-H1B	0.9900	C4-C5	1.5120(14)
C1-H1C	0.9900	C5-H5A	0.9900
O2-C5	1.4100(12)	C5-H5B	0.9900

C4-N1-C3	120.66(8)	N1-C3-C2	112.26(8)
C4-N1-H1A	118.4(9)	N1-C3-H3A	109.2
C3-N1-H1A	120.7(9)	C2-C3-H3A	109.2
C2-C1-C1#1	113.16(10)	N1-C3-H3B	109.2
C2-C1-H1B	108.9	C2-C3-H3B	109.2
C1#1-C1-H1B	108.9	H3A-C3-H3B	107.9
C2-C1-H1C	108.9	O1-C4-N1	122.20(9)
C1#1-C1-H1C	108.9	O1-C4-C5	120.26(9)
H1B-C1-H1C	107.8	N1-C4-C5	117.54(9)
C5-O2-H2A	105.7(9)	O2-C5-C4	113.29(9)
C3-C2-C1	110.78(8)	O2-C5-H5A	108.9
C3-C2-H2B	109.5	C4-C5-H5A	108.9
C1-C2-H2B	109.5	O2-C5-H5B	108.9
C3-C2-H2C	109.5	C4-C5-H5B	108.9
C1-C2-H2C	109.5	H5A-C5-H5B	107.7
H2B-C2-H2C	108.1		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1

Table S16. Torsion angles [°] for 6G

C1#1-C1-C2-C3	-179.40(12)
C4-N1-C3-C2	168.56(10)
C1-C2-C3-N1	-177.53(9)
C3-N1-C4-O1	0.07(16)
C3-N1-C4-C5	179.79(9)
O1-C4-C5-O2	-173.38(9)
N1-C4-C5-O2	6.89(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1

Table S17. Hydrogen bonds for 6G [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1A...O1#2	0.909(2)	2.277(7)	3.1164(11)	153.4(12)
O2-H2A...O1#3	0.863(16)	1.871(16)	2.7334(11)	176.9(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1 #2 x,-y+1,z+1/2 #3 x,-y,z+1/2