Reductive Amination/Cyclization of Methyl Levulinate with Aspartic Acid: Towards Renewable Polyesters with a Rigid Pendant Lactam Unit

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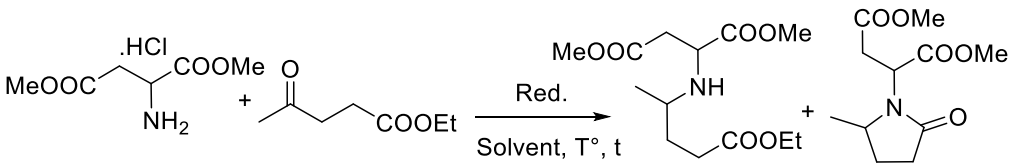
1. General.

Chemicals used in this study have been purchased from Acros Organics and Sigma Aldrich. Solvents were dried by using an MBRAUN Solvent Purification Systems (MB-SPS-800). All reactions were monitored by GC analysis on a Shimadzu. Analytical thin layer chromatography (TLC) was performed on commercial silica gel 60 with fluorescent indicator UV absorbance 254 (Merck). Detection was accomplished by treatment of the plate with dying reagents (potassium permanganate, vanillin or anisaldehyde). Chromatographic purifications were realized on silica gel columns (silica 60 A, 40–63 μm) with a dichloromethane/methanol eluent system. Distillations were conducted with a Kugelrohr apparatus. Polymerization reactions were performed with a Kugelrohr apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer. Chemical shift data are reported in units of δ (ppm) using $CHCl_3$ (δ = 7.26 for ^{1}H NMR spectra and δ = 77.36 for ^{13}C NMR spectra) or DMSO as the internal standard (δ = 2.50 for ^{1}H NMR spectra and δ = 39.52 for ^{13}C NMR spectra). Multiplicities are given as s (singlet), d (double), t (triplet), m (multiplet). Coupling constants, *J*, are reported in Hz. Spectra were fully attributed using -if needed- 2D-NMR (COSY, HSQC, HMBC) spectroscopy. Size exclusion chromatography was performed in THF as eluent at 40°C using a Waters SIS HPLC-pump, a Waters 410 refractometer and Waters styragel columns (HR2, HR3, HR4, HR5E) calibrated with polystyrene standards. TGA analysis were conducted using a Q5000 analyzer from TA Instruments, at 10°C/min under nitrogen (10 mL/min in the balance and 25 mL/min in the oven)**.** High resolution mass spectra (HRMS) were measured on a Waters Synapt G2-Si (mode ESI(+)) at Mass Spectrometry Research Group, (MSRG), University of Mons, Belgium.

2. Additional reductive amination



AspOMe.HCl (1 eq.) **LevOEt (1 eq.)** **1** **2 (DMMPS)**

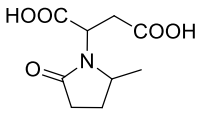
Entry	Reducing system	Solvent, T(°C), t(h)	GC ratio **1**/**2**	Yield (%) (product)[e]
1	$NaBH(OAc)_3$	DCM, 20°C, 15h	100/0	91 (**1**)
2	$NaBH(OAc)_3$	DCM, 50°C, 15 h	95/5	Non isolated
3[a]	$NaBH_4$/AcOH	AcOH, 20°C, 15h	90/10	80 (**1**)
4[a]	$NaBH_4$/AcOH	AcOH, 50°C, 24h	15/85	46 (**2**)
5[b]	HCOOH/NEt_3	DMSO, 100°C, 15h	0/100	25 (**2**)
6[c]	H_2/Pd	H_2O, 70°C, 18h	0/100	17 (**2**)
7[d]	H_2/Pd	H_2O, 70°C, 18h	0/100	21 (**2**)

[a] Two steps procedure: i) $NaBH_4$ in AcOH, R.T., 10 min, then ii) addition of LevOH and AspOMe [b] In a close schlenk tube [c] With LevOH as precursor, in an autoclave under 50 bar of H_2, with 2.5% of Pd 10 wt% on charcoal [d] With 5 equivalents of LevOH [e] Isolated by column chromatography.

Table S1. Reducing system choice for the synthesis of DMMPS

3. Supplementary operating procedures and spectral data for monomers.

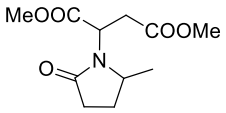
2-(2-Methyl-5-oxopyrrolidin-1-yl)succinic acid (MPSA)



The autoclave was charged with AspOH (0.5 g, 3.76 mmol), LevOMe (2.3 mL, 18.80 mmol), Pd 10 wt% on charcoal (100 mg, 0.09 mmol) and methanol. The autoclave was sealed, purged three times with hydrogen, and then pressured at 50 bar of H_2. The reaction mixture was stirred for 24 h at 70 °C. After cool down to room temperature and depressurization, the reaction mixture was filtered on a short pad of Celite® to remove catalyst, then concentrated under reduced pressure. The residue was taken in 30 mL of water, and extracted three times with organic solvent (DCM or AcOEt) (3 x 20 mL) to remove the excess of LevOMe. The aqueous layer was concentrated under reduced pressure. The resultant viscous oil was dried under reduced pressure for several hours to afford the pure diacid **MPSA** as a highly hygroscopic white powder (0.79 g starting from 0.5 of AspOH, 95% yield). The compound is obtained as a mixture of diastereomers (noted Major (*M*)/minor (*m*), 70:30).

^{1}H NMR (300 MHz, D_2O, 300 K): δ (ppm) = 1.21 (d, ^{3}J= 6.3 Hz, 0.90H, -CH-C***H***$_3$(*m*)), 1.27 (d, ^{3}J= 6.3 Hz, 2.10H, -CH-C***H***$_3$(*M*)), 1.60-1.82 (m, 1H, -C***H***$_2$-CH-CH_3), 2.17-2.53 (m, 3H, -C***H***$_2$-CH-CH_3 and -C***H***$_2$-CO-N-), 2.78-2.94 (m, 1H, -C***H***$_2$-COOH), 3.07-3.25 (m, 1H, -CH-C**H**$_2$-COOH), 3.79-4.02 (m, 1H, -C***H***-CH_3-), 4.57 (t, ^{3}J = 7.2 Hz, 0.7H, -C***H***-COOH (*M*)), 4.77 (m, 0.3H, -C***H***-COOH (*M*), hidden by the D_2O peak).

Dimethyl 2-(2-methyl-5-oxopyrrolidin-1-yl)succinate (DMMPS)



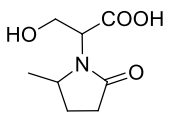
The MPSA (0.79 g, 3.67 mmol) was dissolved in MeOH (10 mL) and sulfuric acid (0.2 mL, 0.37 mmol) was added. The mixture was heated to reflux for 16 hours. After evaporation of the methanol, the mixture was dissolved in CH_2Cl_2 (30 mL), and washed with a saturated solution of sodium hydrogen carbonate (20 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure. The resulting oil was subjected to distillation using a kugelrohr distillation apparatus (100 °C, 0.15 mbar) to afford the pure diester as a colourless oil (794 mg, 89% yield).
The compound is obtained as a mixture of diastereomers (noted Major (*M*)/minor (*m*), 69:31).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.20 (d, ^{3}J = 6.3 Hz, 0.85H, -CH-C***H***$_3$(*m*)), 1.27 (d, ^{3}J= 6.3 Hz, 2.15H, -CH-C***H***$_3$(*M*)), 1.56-1.73 (m, 1H, -C***H***$_2$-CH-CH_3), 2.16-2.47 (m, 3H, -C***H***$_2$-CH-CH_3 and -C***H***$_2$-CO-N-), 2.79 (dd, ^{2}J = 16.4 Hz, ^{3}J= 7.3 Hz, 0.34H, -C***H***$_2$-CO_2CH_3 (*m*)), 2.96 (dd, ^{2}J= 17.0, ^{3}J = 8.1 Hz, 0.66H, -C***H***$_2$-CO_2CH_3 (*M*)), 3.18 (dd, ^{2}J = 17.0 Hz, ^{3}J= 5.9 Hz, 0.66H, -C***H***$_2$-CO_2CH_3 (*M*)), 3.27 (dd, ^{2}J= 16.4 Hz, ^{3}J= 6.9 Hz, 0.34H, -C***H***$_2$-CO_2CH_3 (*m*)), 3.64-3.74 (4s, 6H, -O-C***H***$_3$), 3.74-3.87 (m, 1H, -C***H***-CH_3-), 4.47 (dd, ^{3}J = 8.1, 5.9 Hz, 0.66H, -C***H***-CO_2CH_3 (*M*)), 4.66 (dd, 2 x ^{3}J = 7.1 Hz , 0.34H, -C***H***-CO_2CH_3 (*m*)).

^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 19.9 (-CH-***C***H_3, (*M*)), 20.0 (-CH-***C***H_3, (*m*)), 27.1 (-***C***H_2-CH-CH_3, (*M*)), 27.3 (-***C***H_2-CH-CH_3, (*m*)), 29.3 (-***C***H_2-CO-N-, (*M*)), 29.8 (-***C***H_2-CO-N-, (*m*)), 33.9 (-***C***H_2-CO_2CH_3, (*M*)), 34.0 (-***C***H_2-CO_2CH_3, (*M*)), 51.1 (-***C***H-CO_2CH_3, (*m*)), 51.3 (2C, -***C***H-CO_2CH_3, (*M*)), 51.6 (O-***C***H_3, (*m*) and (*M*)), 52.3 (O-***C***H_3, (*m*)), 52.4 (O-***C***H_3, (*M*)), 54.4 (-N-***C***H-CH_3, (*m*)), 54.8 (-N-***C***H-CH_3, (*M*)), 169.8 (-***C***=O, (*M*)), 170.5 (-***C***=O, (*m*)), 170.9 (-***C***=O, (*m*)), 171.4 (-***C***=O, (*M*)), 174.6 (-***C***=O, (*M*)), 175.9 (-***C***=O, (*m*)).

HRMS m/z calcd. for $C_{11}H_{17}NO_5Na$: 266.1004 $[M+Na]^+$; found: 266.1005.

3-Hydroxy-2-(2-methyl-5-oxopyrrolidin-1-yl)propanoic acid (HMPPA)



The autoclave (300 mL mechanically stirred Parr stainless-steel autoclave) was charged with SerOH (5 g, 47.6 mmol), LevOMe (17.7 mL, 143 mmol), Pd 10 wt% on charcoal (1.27 g, 1.19 mmol) and methanol (100 mL). The autoclave was sealed, purged three times

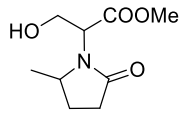
with hydrogen, and then pressured at 50 bar of H_2. The reaction mixture was stirred for 24 h at 70 °C. After cool down to room temperature and depressurization, the reaction mixture was filtered on a short pad of Celite® to remove catalyst, then concentrated under reduced pressure. The residue was taken in 100 mL of water, and extracted three times with DCM (3 x 100 mL) to remove the excess of LevOMe. The aqueous layer was concentrated under reduced pressure. The resultant viscous oil was dried under reduced pressure for several hours to afford the pure hydroxy-acid as a white solid (8.56 g, 95%). The compound is obtained as a mixture of diastereomers (noted Major (*M*)/minor (*m*), 69:31)

^{1}H NMR (300 MHz, D_2O, 300 K): δ (ppm) = 1.25-1.34 (d, x2 superimposed, ^3J = 6.5 Hz, 3H, -C***H***$_3$), 1.70-1.87 (m, 1H, -C***H***$_2$-CH-CH$_3$), 2.29-2.66 (m, 3H, -C***H***$_2$-CH-CH$_3$ and -C***H***$_2$-CO-N), 3.91-4.19 (m, 3H, -C***H***-CH$_3$ and -C***H***$_2$-OH), 4.37 (dd, ^3J = 8.1 Hz, 5.2 Hz, 0.69H, -C***H***-COOH (*M*)), 4.52 (dd, ^3J = 8.3 Hz, 5.0 Hz, 0.69H, -C***H***-COOH (*m*)).

^{13}C NMR (75 MHz, D_2O, 300 K): δ (ppm) = 19.0 (-CH-***C***H$_3$ (*M*)), 19.3 (-CH-***C***H$_3$ (*m*)), 26.5 (-***C***H$_2$-CH-CH$_3$ (*M*)), 26.6 (-***C***H$_2$-CH-CH$_3$ (*m*)), 29.7 (-***C***H$_2$-CO-N- (*M*)), 30.0 (-***C***H$_2$-CO-N- (*m*)), 55.7 (-***C***H- (*m*)), 56.6 (-***C***H- (*m*)), 57.0 (-***C***H- (*M*)), 57.2 (-***C***H- (*M*)), 58.5 (-***C***H$_2$-OH (*m*)), 59.4 (-***C***H$_2$-OH (*M*)), 172.2 (-***C***O-OMe (*M*)), 172.7 (-***C***-OMe (*m*)), 178.6 (-***C***O-N- (*M*)), 179.6 (-***C***O-N- (*m*)).

HRMS m/z calcd. for $C_8H_{14}NO_4$: 188.0923 $[M+H]^+$; found: 188.0919.

2-(2-Methyl-5-oxopyrrolidin-1-yl)succinic acid (MHMPP)



The **2-**(2-methyl-5-oxopyrrolidin-1-yl)succinic acid (8.56 g, 45.7 mmol) was dissolved in MeOH (100 mL) and sulfuric acid (0.25 mL, 4.57 mmol) was added. The mixture was heated to reflux for 16 hours. After evaporation of the methanol, the mixture was dissolved in DCM (100 mL), and washed with a saturated solution of sodium hydrogen carbonate (50 mL). The organic layer was dried with magnesium sulphate and concentrated under reduced pressure. The resulting oil was subject to silica gel column chromatography (DCM/MeOH, 99:1) to afford the pure compound as colourless oil which crystallized after several hours (7.66 g, 83%). The compound is obtained as a mixture of diastereomers (noted Major (*M*)/minor (*m*) 7:3)

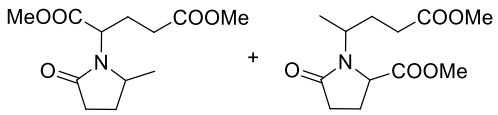
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.16 and 1.18 (d, x2 superimposed, ^3J = 6.5 Hz, 3H, -C***H***$_3$), 1.53-1.73 (m, 1H, -C***H***$_2$-CH-CH$_3$), 2.18-2.52 (m, 3H, -C***H***$_2$-CH-CH$_3$ and -C***H***$_2$-CO-N-), 3.70 (s, 3H, -OCH$_3$), 3.72-3.79 (m, 1H, -C***H***-CH$_3$), 3.88-4.06 (m, 2H, -C***H***$_2$-OH),4.06-4.13 (m, 1H, -C***H***-COOMe), 4.23 (m broad, 0.63, -O*H* (*M*)), 4.66 (m broad, 0.28, -O*H* (*m*)).

^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 20.0 (-CH-***C***H$_3$ (*m*)), 20.1 (-CH-***C***H$_3$ (*M*)), 27.3 (-***C***H$_2$-CH-CH$_3$ (*M*)), 27.5 (-***C***H$_2$-CH-CH$_3$ (*m*)), 29.8 (-***C***H$_2$-CO-N- (*M*)), 30.4 (-***C***H$_2$-CO-N- (*m*)), 52.4 (-OCH$_3$ (*M*)), 52.5 (-OCH$_3$), 55.6 (-***C***H- (*m*)), 56.3 (-***C***H- (*m*)), 58.2 (-***C***H- (*m*)), 58.3

(-***C***H- (*M*)), 61.4 (-***C***H_2-OH (*M*)), 61.5 (-***C***H_2-OH (*M*)), 169.6 (-***C***O-OMe (*m*)),169.9 (-***C***-OMe (*M*)), 176.2 (-***C***O-N- (*M*)), 177.5 (-***C***O-N- (*m*)).

HRMS m/z calcd. for $C_9H_{15}NO_4Na$: 224.0899 $[M+Na]^+$; found: 224.0897.

Dimethyl 2-(2-methyl-5-oxopyrrolidin-1-yl)pentanedioate (3 - DMMPG) + methyl 1-(5-methoxy-5-oxopentan-2-yl)-5-oxopyrrolidine-2-carboxylate (4).



The autoclave (300 mL mechanically stirred Parr stainless-steel autoclave) was charged with GluOH (0.5 g, 47.6 mmol), LevOMe (17.7 mL, 143 mmol), Pd 10 wt% on charcoal (1.27 g, 1.19 mmol) and methanol (100 mL). The autoclave was sealed, purged three times with hydrogen, and then pressured at 50 bar of H_2. The reaction mixture was stirred for 24 h at 70 °C. After cool down to room temperature and depressurization, the reaction mixture was filtered on a short pad of Celite® to remove catalyst, then concentrated under reduced pressure. The residue was taken in 100 mL of water, and extracted three times with DCM (3 x 100 mL) to remove the excess of LevOMe. The aqueous layer was concentrated under reduce pressure. The resultant viscous oil was dried under reduced pressure for several hours. The mixture was dissolved in MeOH (100 mL) and sulfuric acid (0.25 mL, 4.57 mmol) was added. The mixture was heated to reflux for 16 hours. After evaporation of the methanol, the mixture was dissolved in DCM (100 mL), and washed with a saturated solution of sodium hydrogen carbonate (50 mL). The organic layer was dried with magnesium sulphate and concentrated under reduced pressure. The resulting oil was distillated using a Kugelrohr distillation apparatus (120°C, 0.10 mbar) to afford the pure compound as colourless oil which crystallized after several hours (7.66 g, 83% yield).

^{1}H NMR: see figure S10

HRMS m/z calcd. for $C_{12}H_{19}NO_5Na$: 280.1161 $[M+Na]^+$; found: 280.1158.

4. Visual outlook of the polyesters

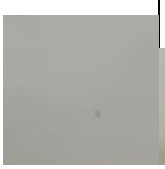
PHMPS (hexanediol)	**PPeMPS (pentanediol)**	**PBMPS (butanediol)**	**PPMPS (propanediol)**	**PEMPS (ethyleneglycol)**
				

Table S2. Visual outlook of the polyesters

5. ^{1}H and ^{13}C NMR spectra and GC chromatogram of monomers

Monomers:

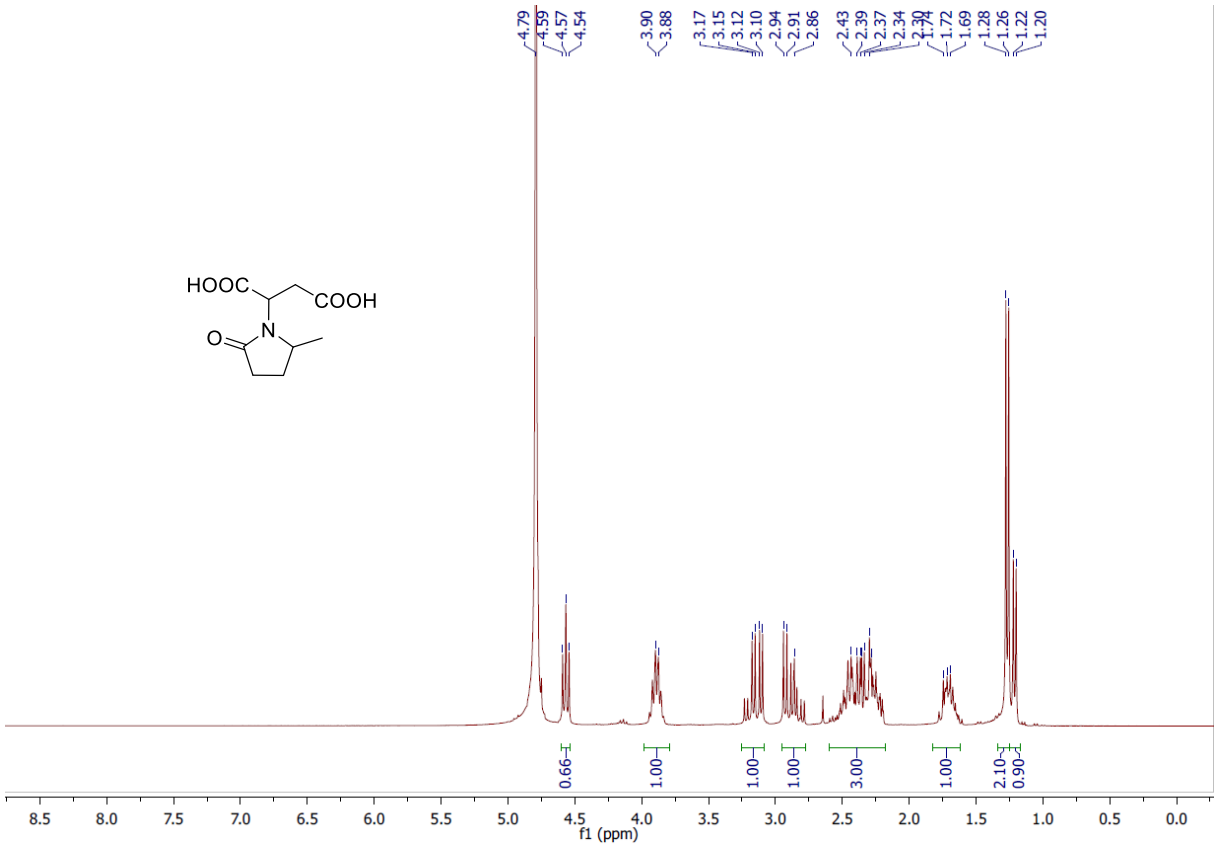


Figure S1. ^{1}H NMR Spectra of **MPSA** (D_2O, 300 MHz and 75 MHz, 300 K)

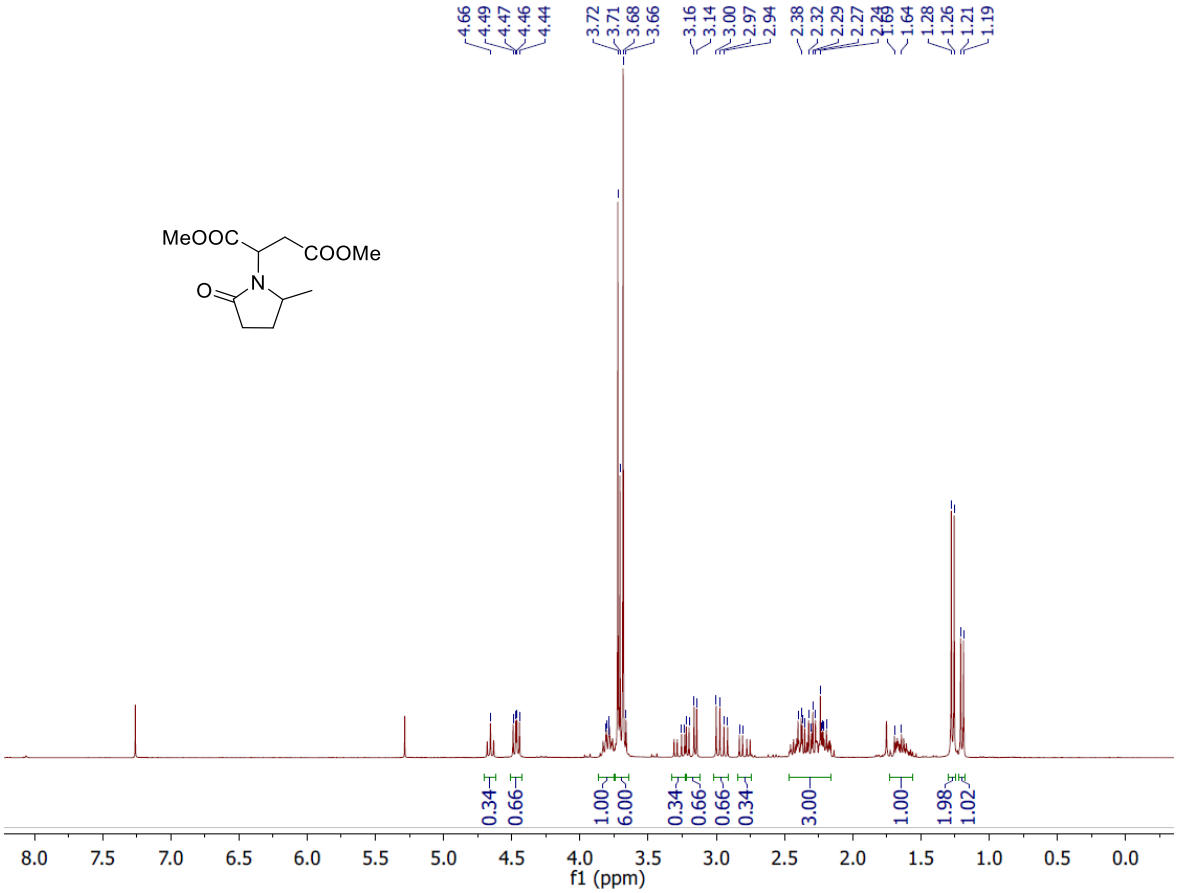


Figure S2. ^{1}H NMR Spectra of **DMMPS** ($CDCl_3$, 300 MHz, 300 K)

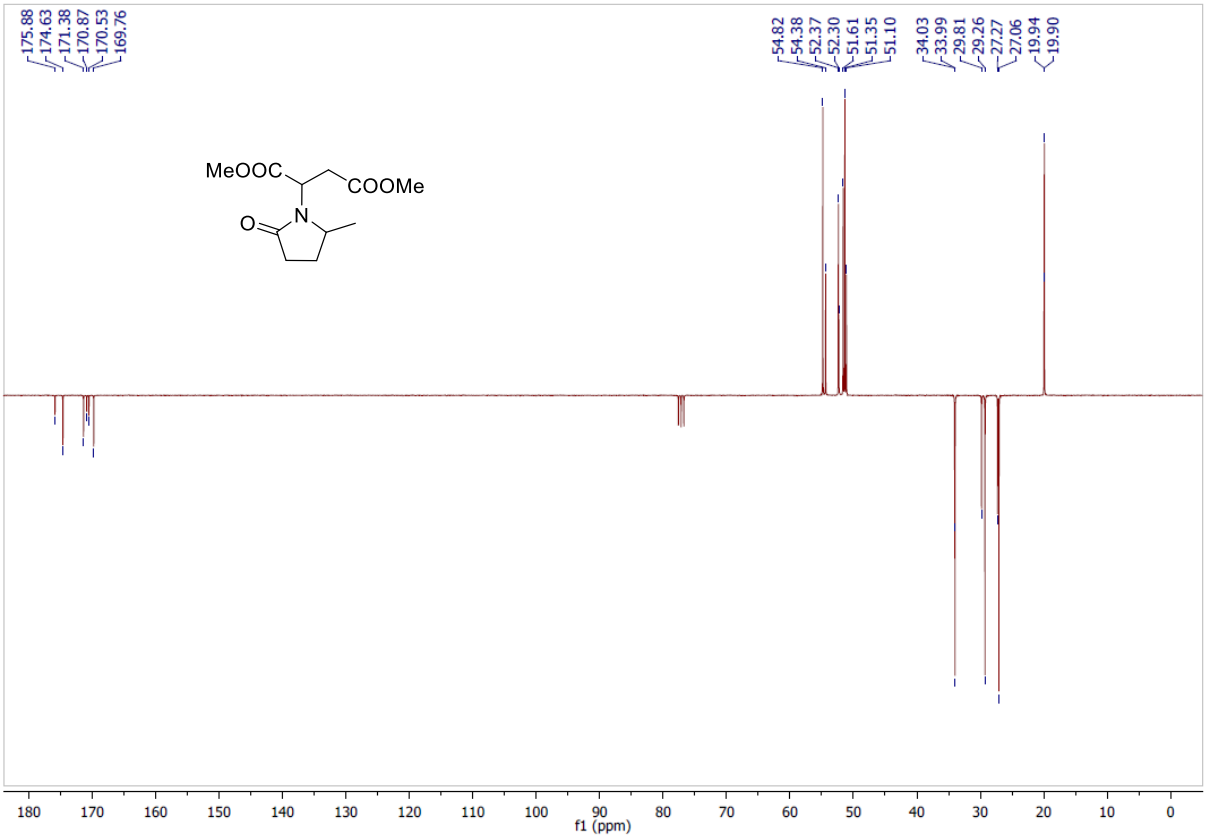


Figure S3. ^{13}C NMR Spectra of **DMMPS** ($CDCl_3$, 75 MHz, 300 K)

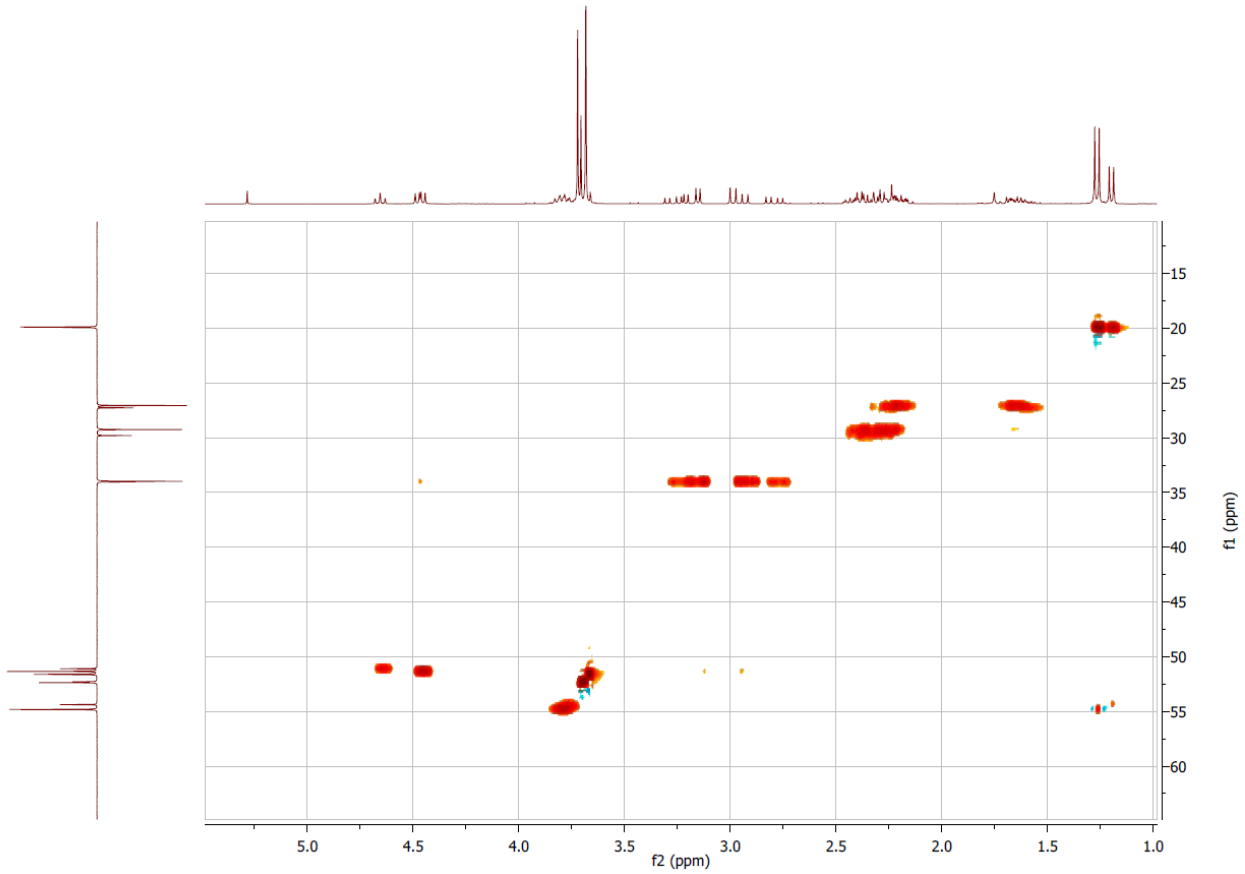


Figure S4. 2D-HSQC NMR Spectra of **DMMPS** ($CDCl_3$, 300 MHz / 75 MHz, 300 K)

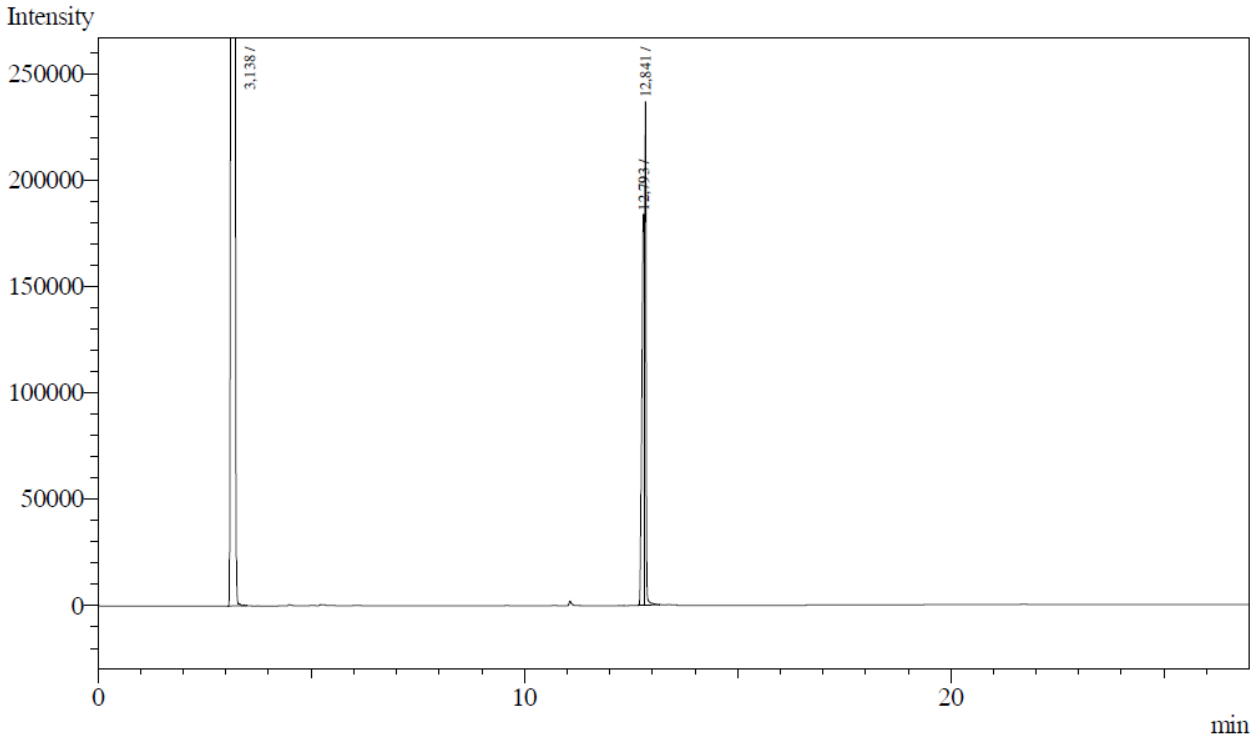


Figure S5. GC chromatogram of **DMMPS**

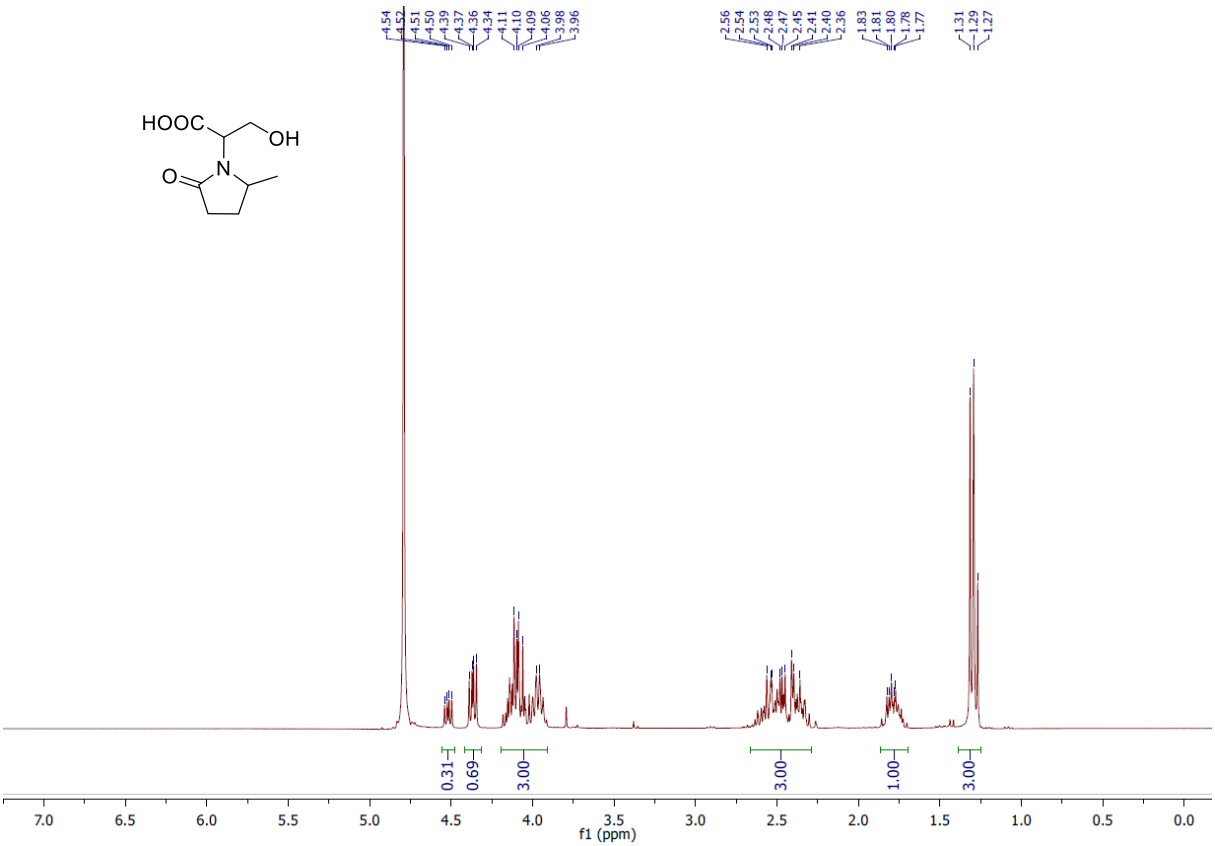


Figure S6. ^{1}H NMR Spectra of **HMPPA** ($CDCl_3$, 300 MHz, 300 K)

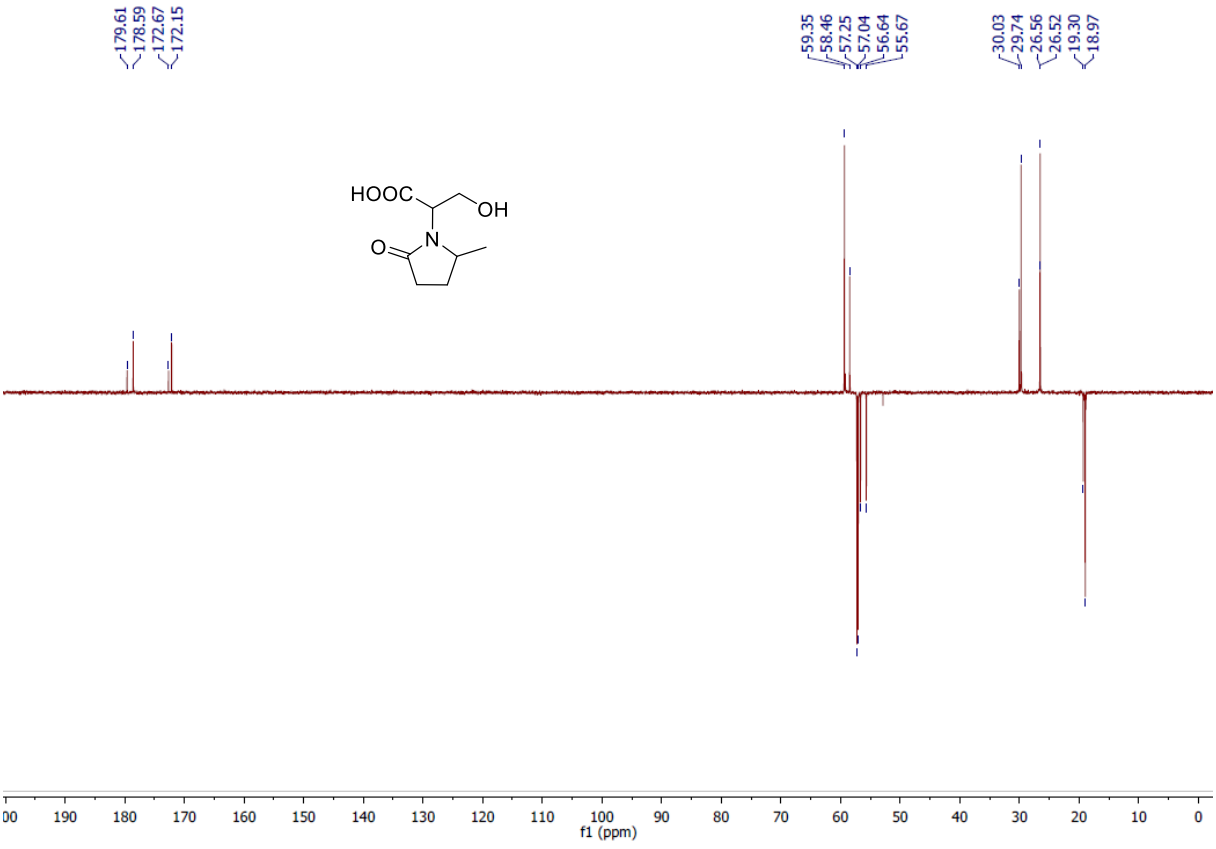


Figure S7. ^{13}C NMR Spectra of **HMPPA** ($CDCl_3$, 75 MHz, 300 K)

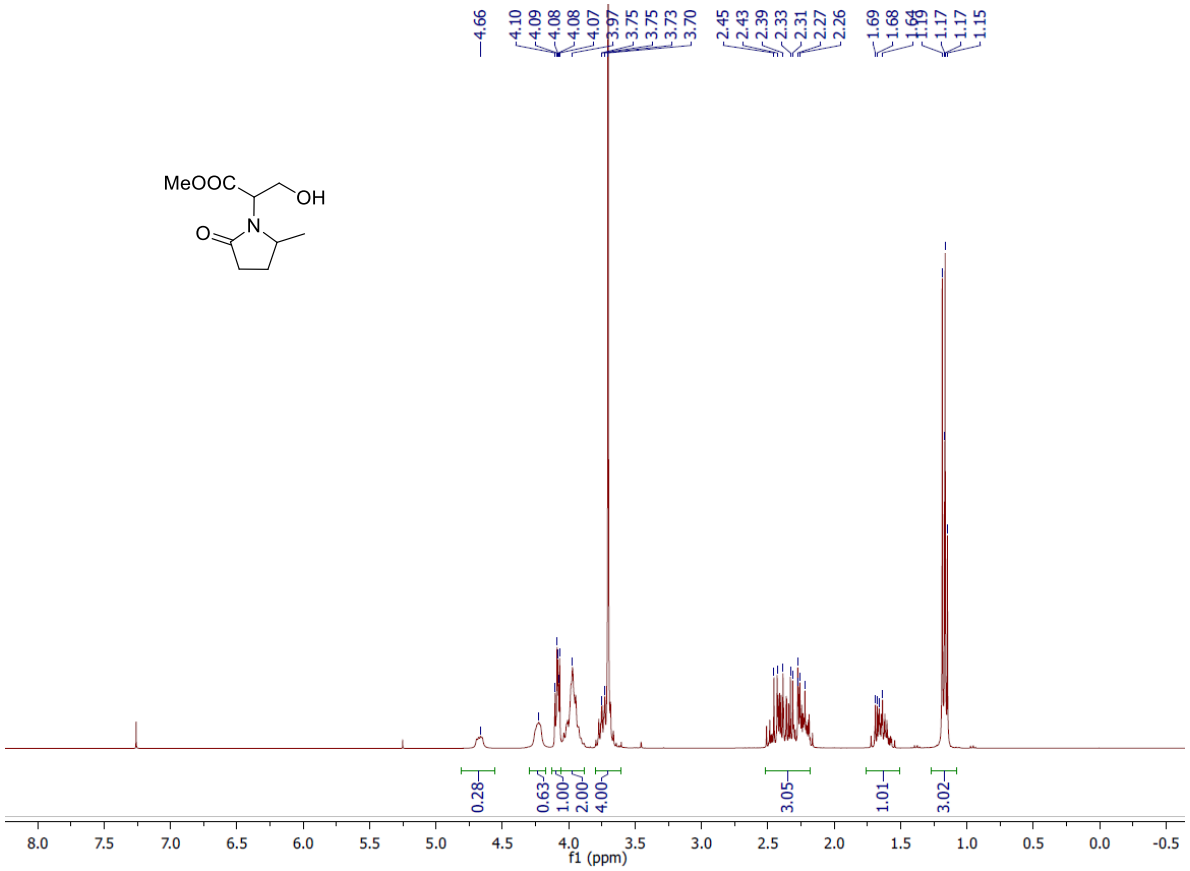


Figure S8. ^{1}H NMR Spectra of **MHMPP** ($CDCl_3$, 300 MHz, 300 K)

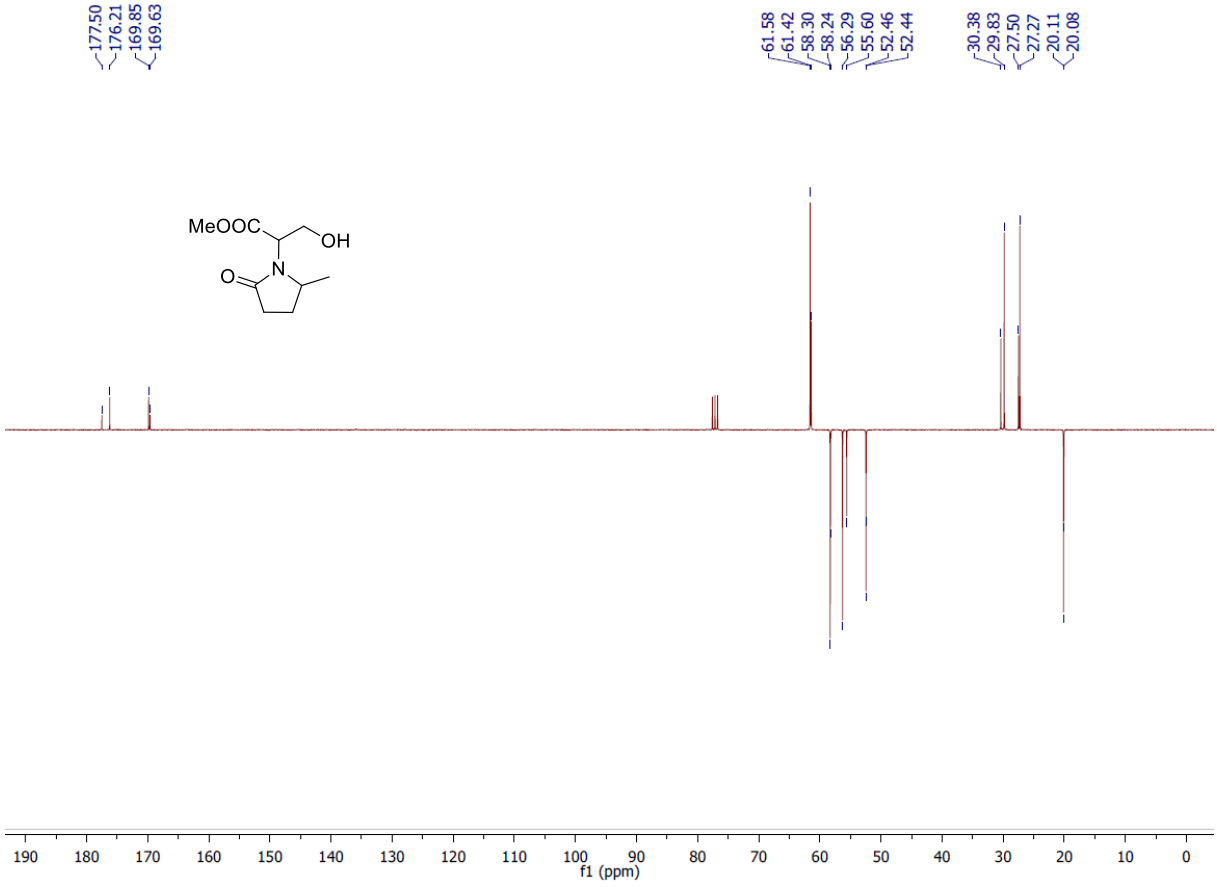


Figure S9. ^{13}C NMR Spectra of **MHMPP** ($CDCl_3$, 75 MHz, 300 K)

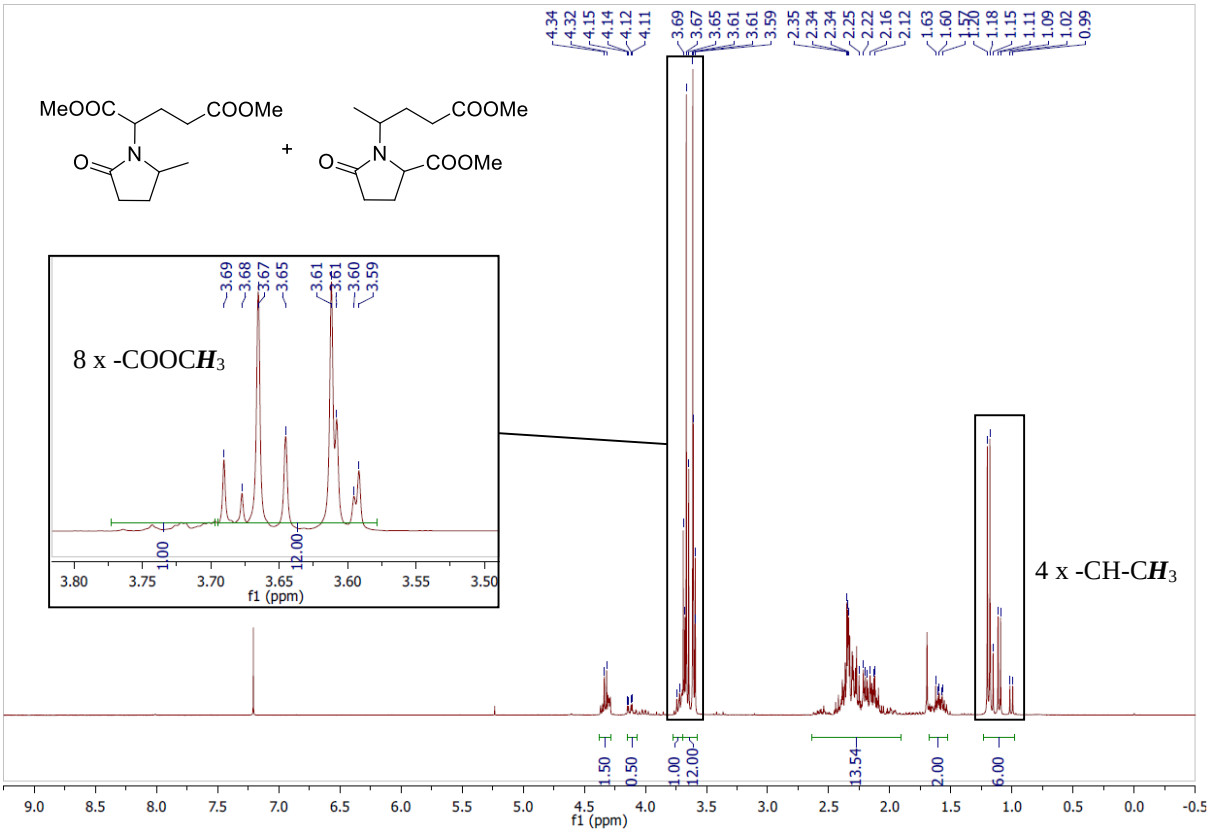


Figure S10. ^{1}H NMR Spectra of the mixture **3 + 4** synthesized from GluOH ($CDCl_3$, 300 MHz, 300 K)

Polymerisation trial with MHMPP:

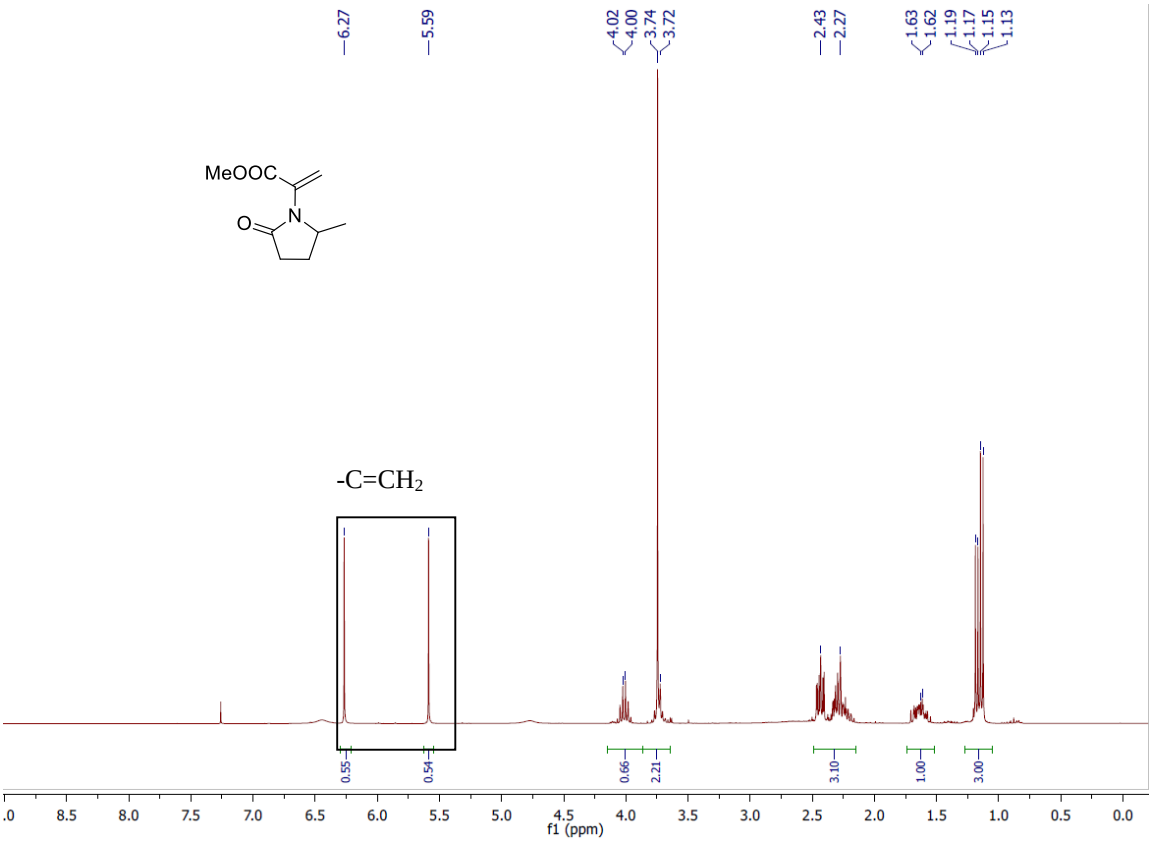


Figure S11. ^{1}H NMR Spectra of the mixture evaporated from the bulk ($CDCl_3$, 300 MHz, 300 K)

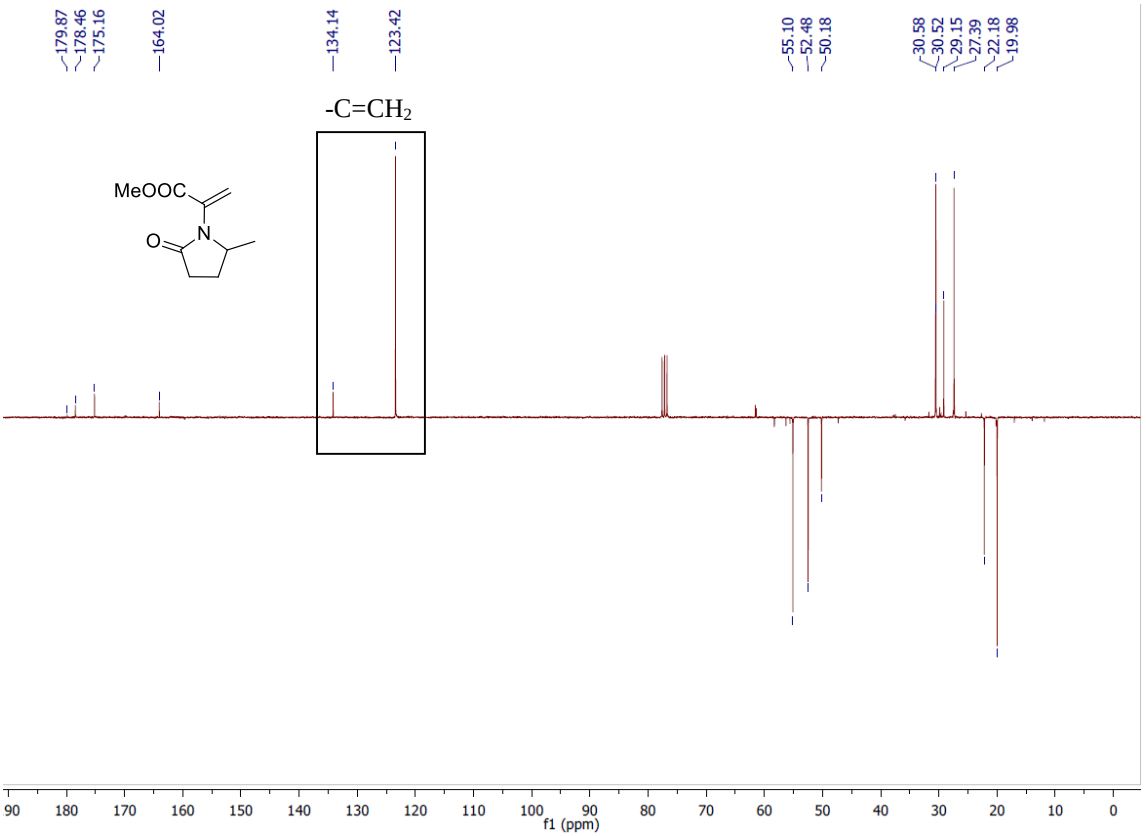
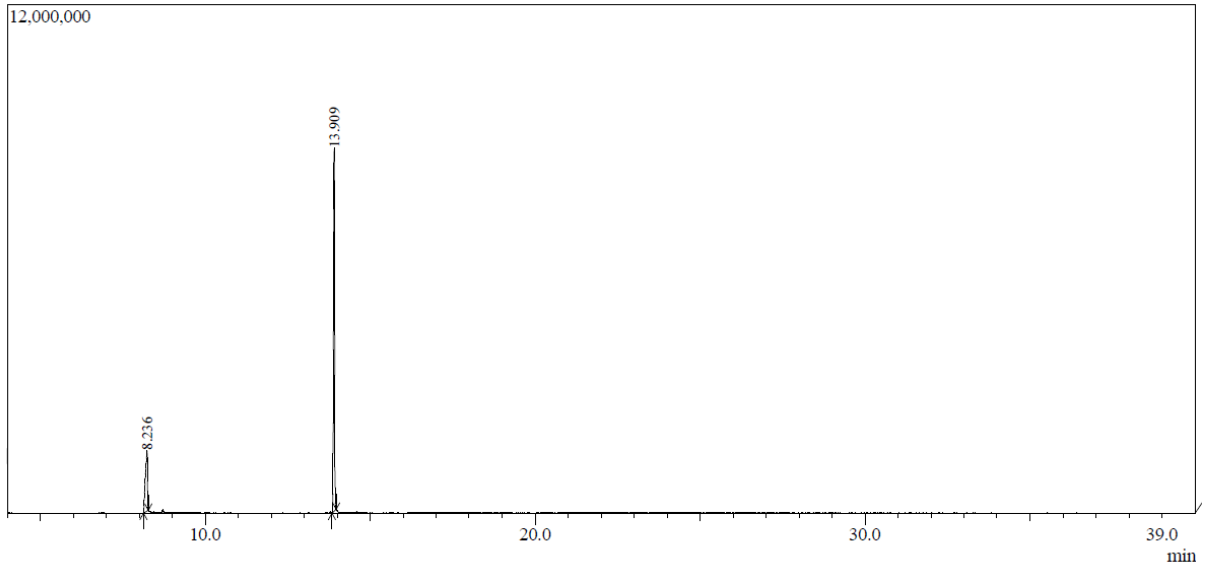


Figure S12. ^{13}C NMR Spectra of the mixture evaporated from the bulk ($CDCl_3$, 75 MHz, 300 K)



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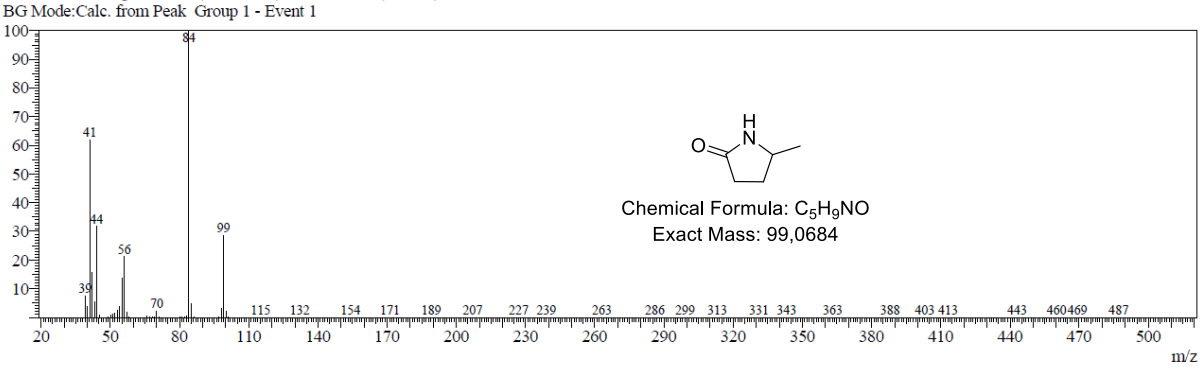
RawMode:Averaged 8.2-8.2(1271-1273) BasePeak:84(442709)
BG Mode:Calc. from Peak Group 1 - Event 1



Line#:2 R.Time:13.9(Scan#:2974)
MassPeaks:322
RawMode:Averaged 13.9-13.9(2973-2975) BasePeak:96(690513)
BG Mode:Calc. from Peak Group 1 - Event 1

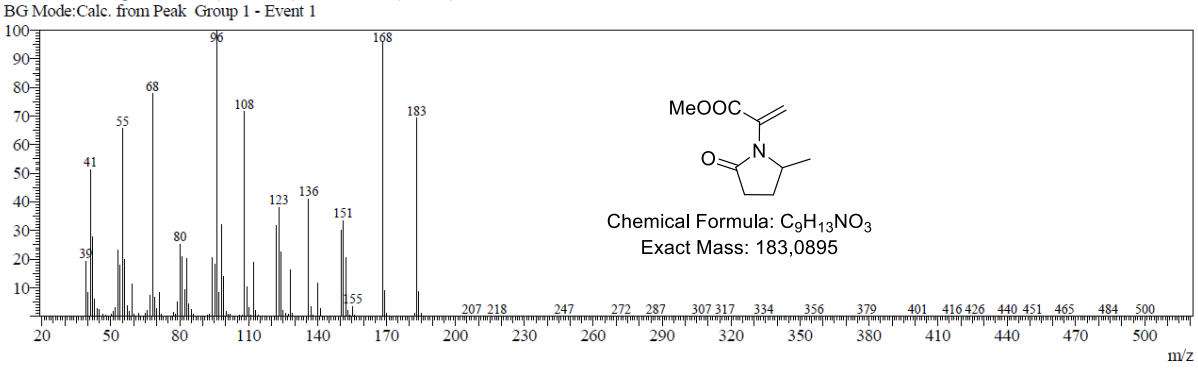


Figure S13. GC-MS chromatogram of the mixture evaporated from the bulk

1. ^{1}H and ^{13}C NMR spectra, FTIR chromatograms, GPC, DSC and ATG curves of polymers

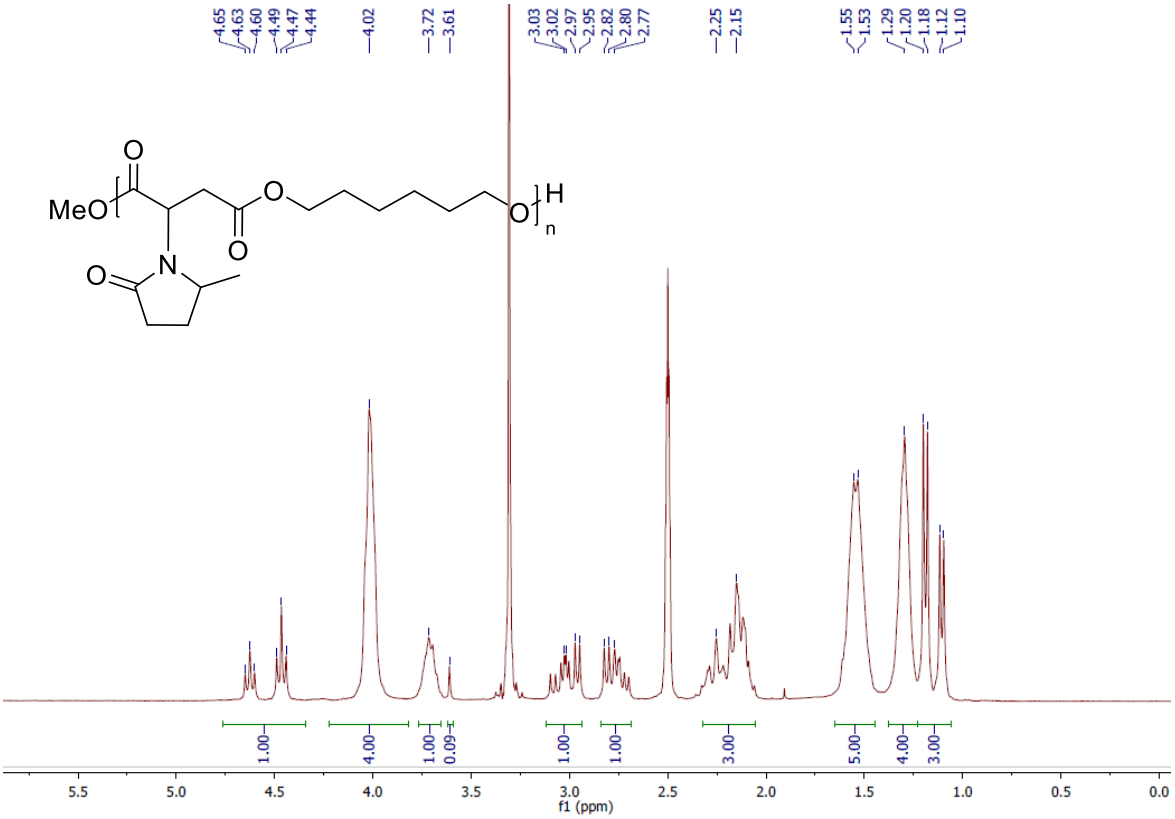


Figure S14. ^{1}H NMR Spectrum of **PHMPS** (DMSO-d_6, 300 MHz, 300 K)

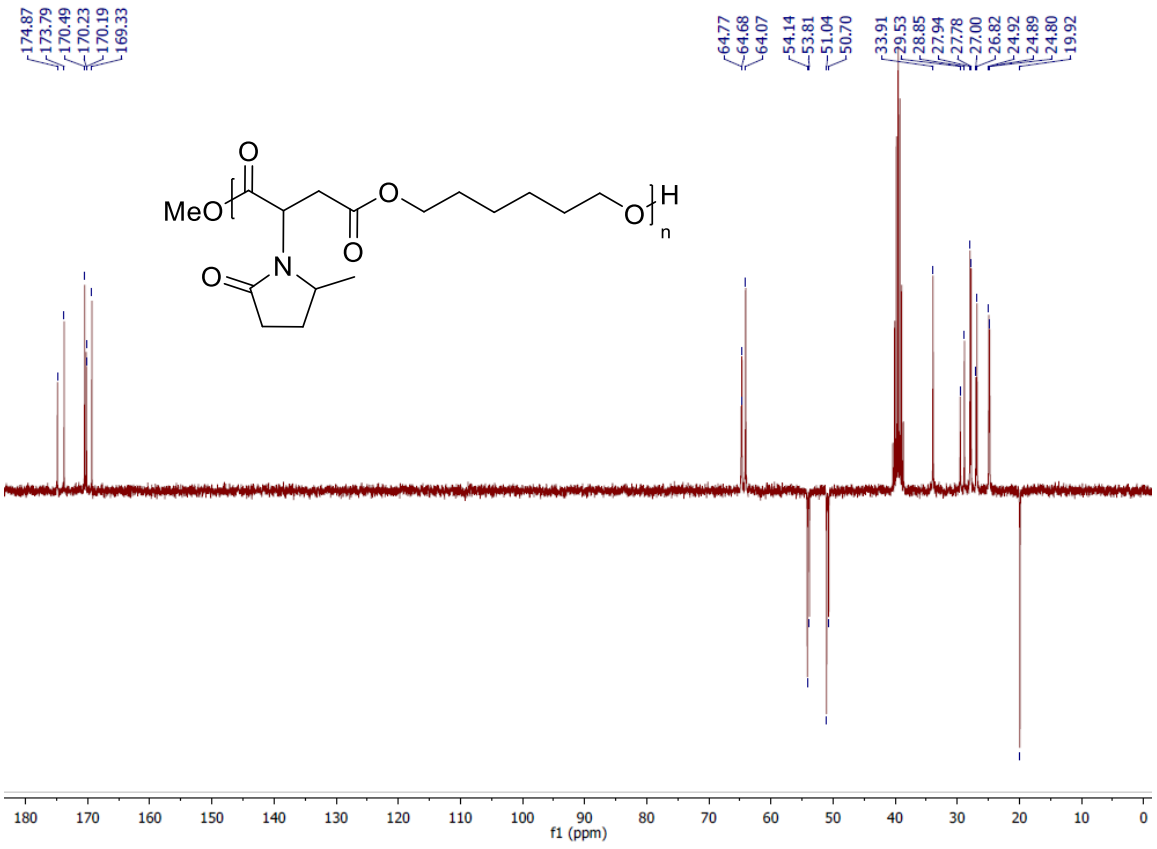


Figure S15. ^{13}C NMR Spectrum of **PHMPS** (DMSO-d_6, 75 MHz, 300 K)

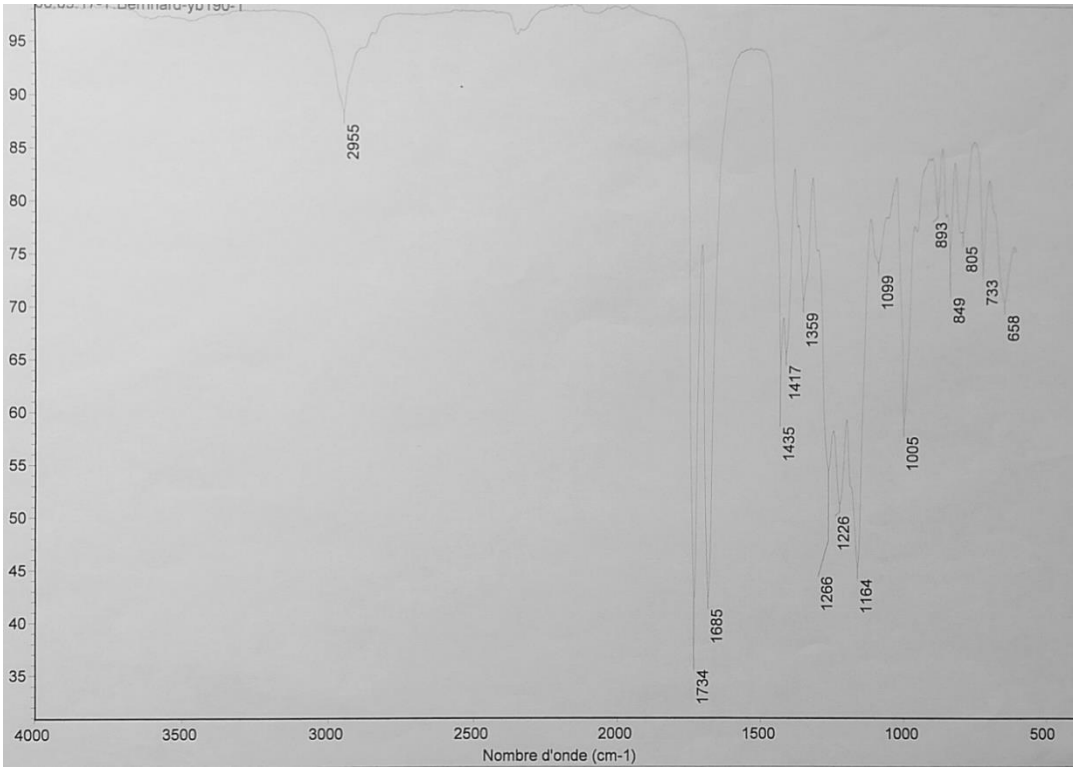
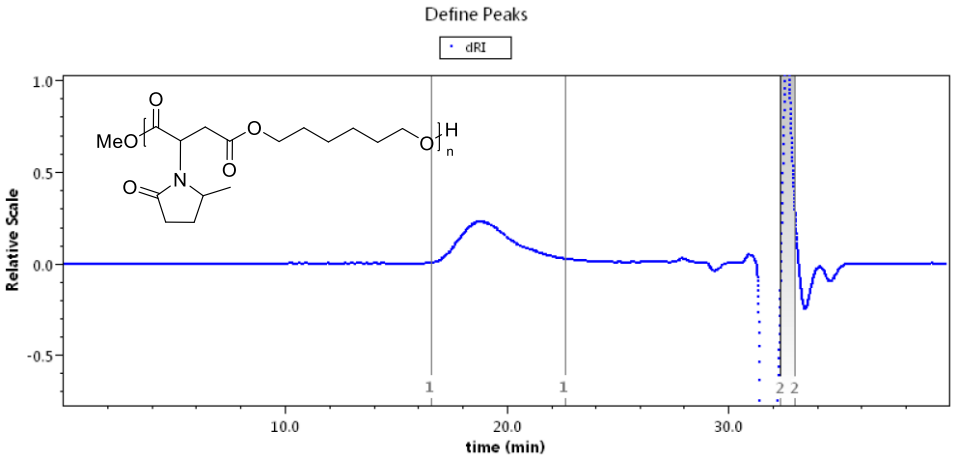


Figure S16. FTIR spectrum of **PHMPS**



Peak Results

	Peak 1
Masses	
Calculated Mass (µg)	122.09
Molar mass moments (g/mol)	
Mn	2.051×10^{4} (±6.896%)
Mw	3.441×10^{4} (±6.896%)
Mz	5.210×10^{4} (±15.420%)
M(avg)	8.743×10^{3} (±0.347%)
Polydispersity	
Mw/Mn	1.678 (±9.752%)
Mz/Mn	2.540 (±16.892%)

Figure S17. GPC curve and data of **PHMPS** (40°C, THF, PS as standard)

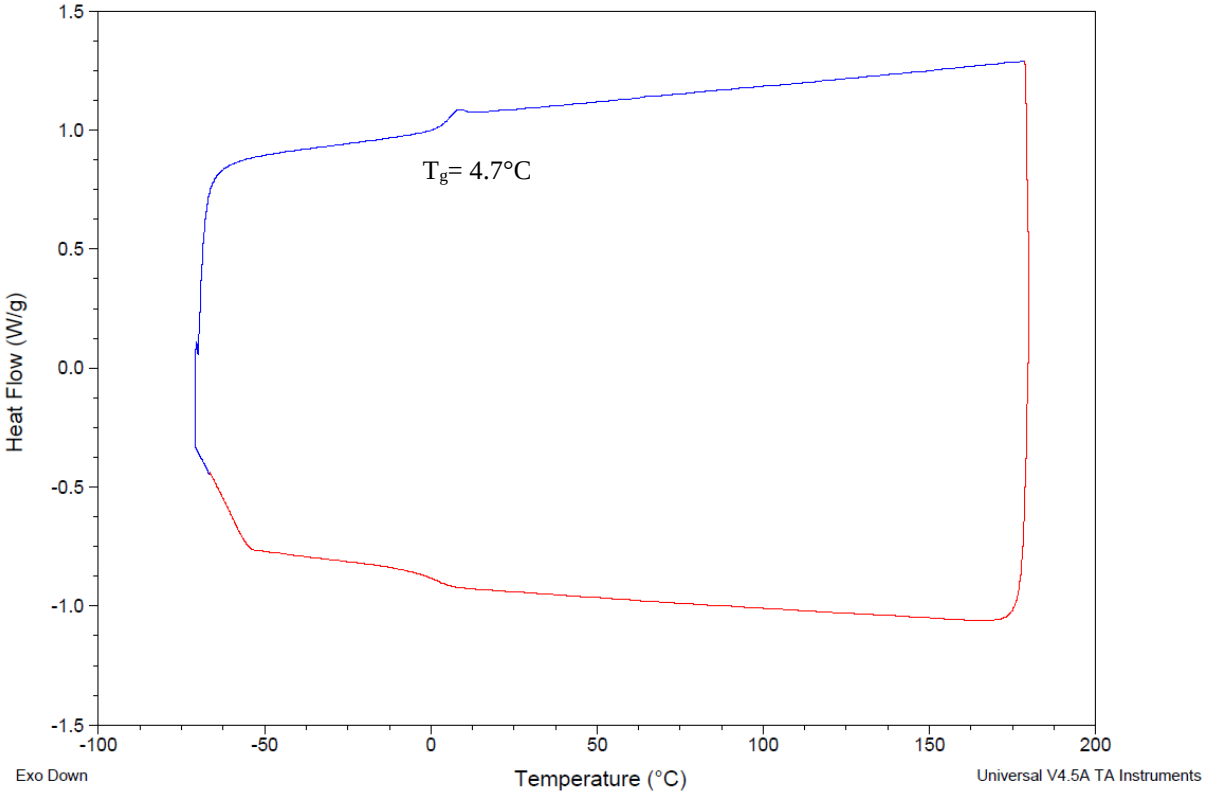


Figure S18. Second heating and cool down DSC curve of **PHMPS** (10°C/min, exo down)

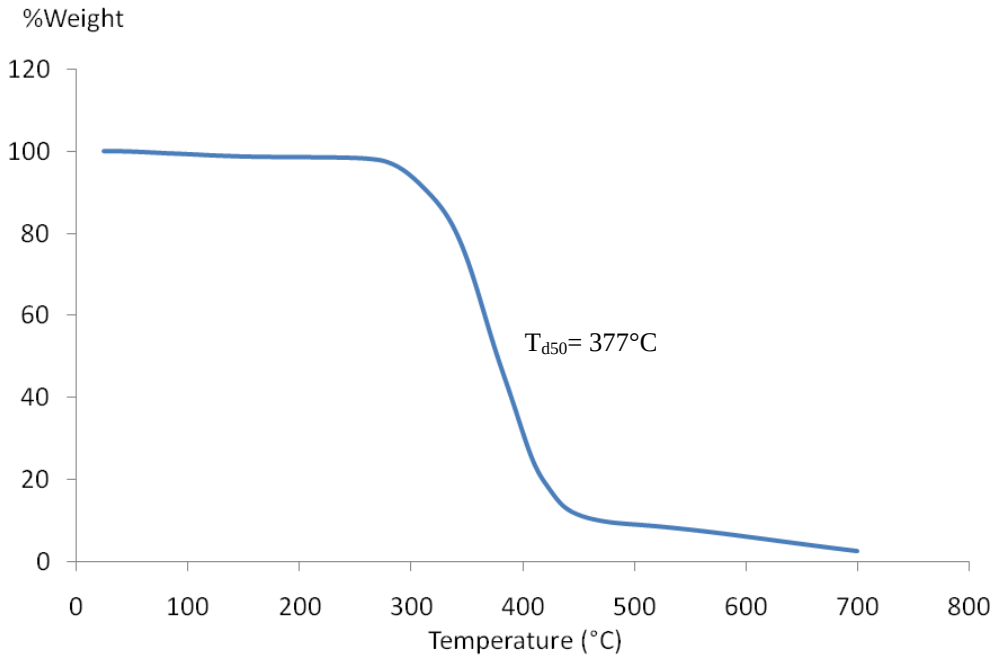


Figure S19. ATG curve of **PHMPS** (10°C/min, under N_2)

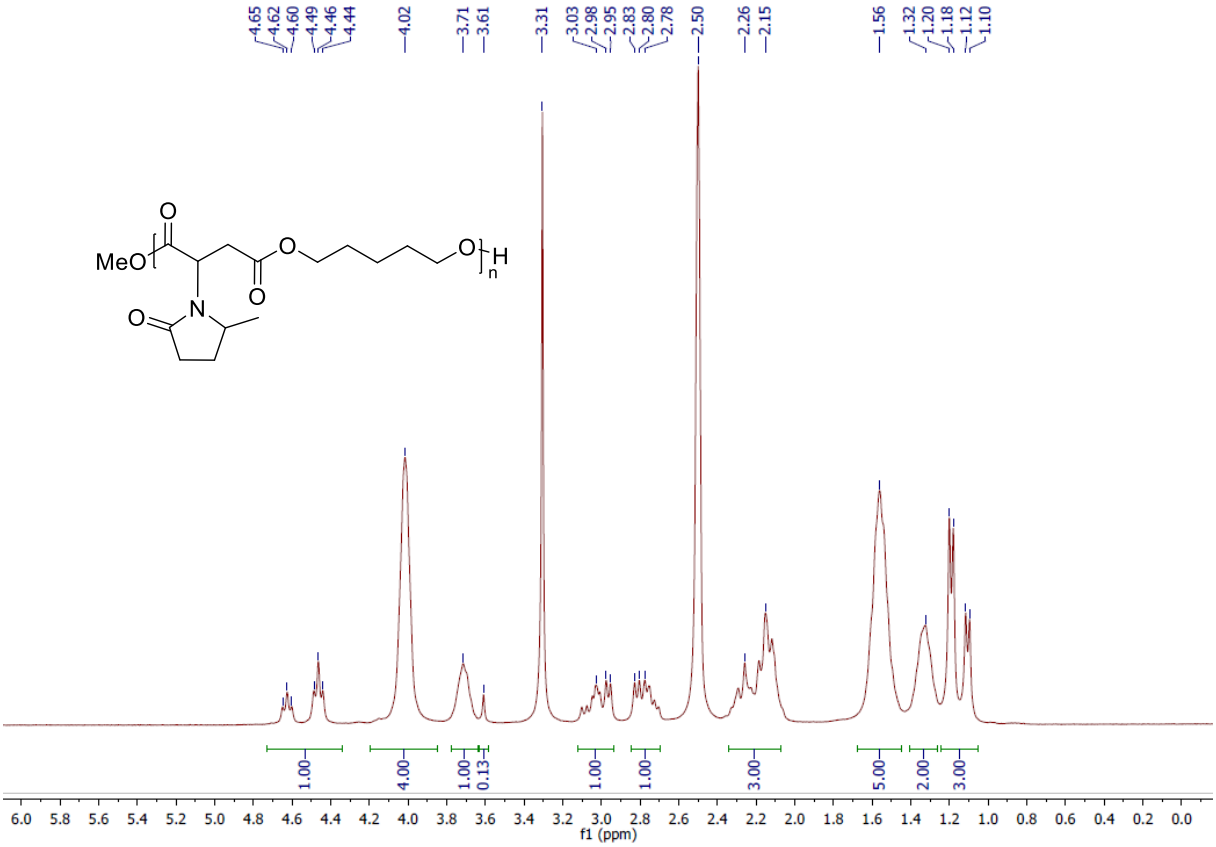


Figure S20. ^{1}H NMR Spectrum of **PPeMPS** (DMSO-d_6, 300 MHz, 300 K)

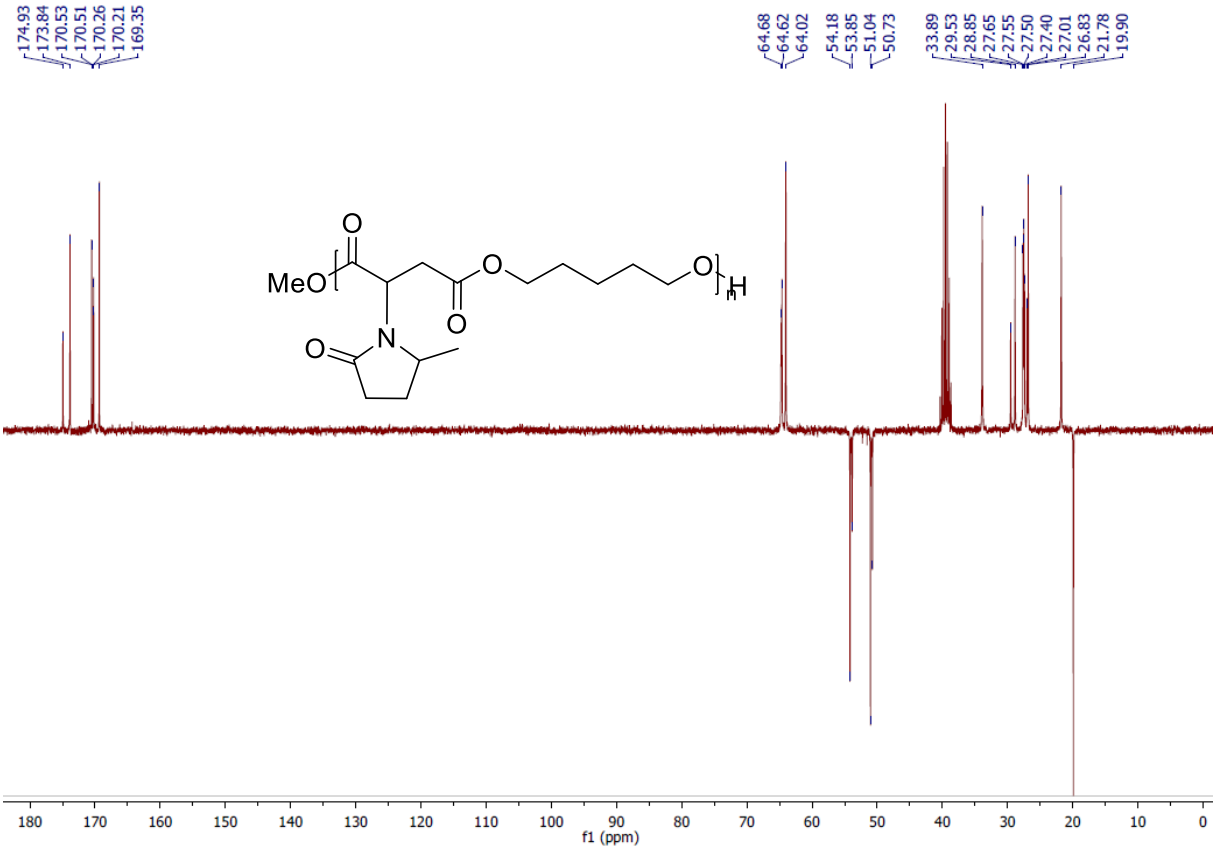
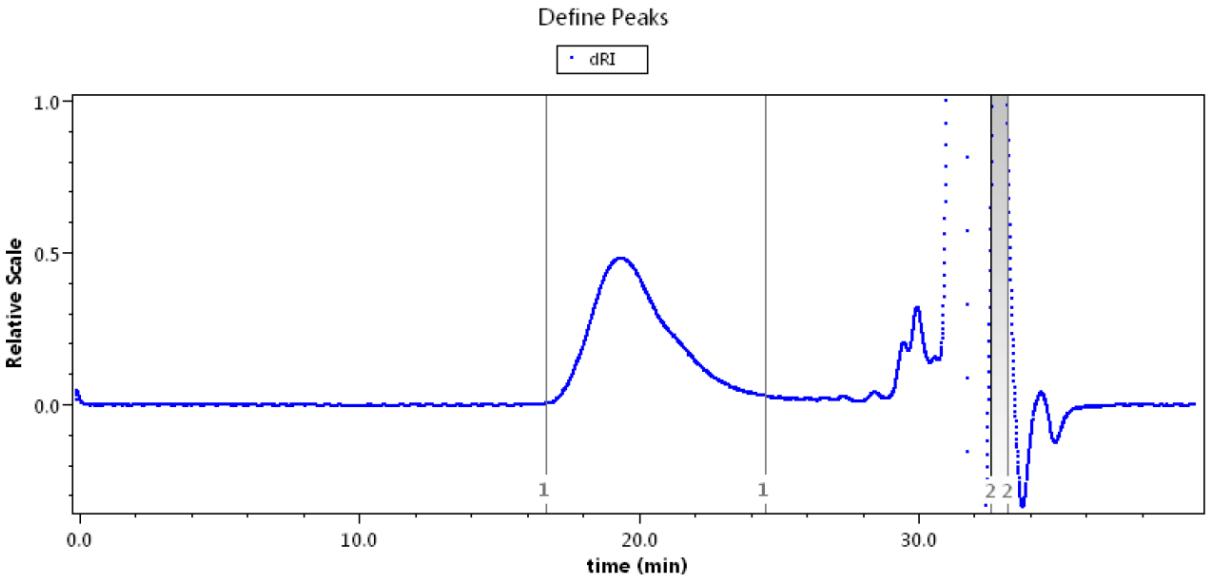


Figure S21. ^{13}C NMR Spectrum of **PPeMPS** (DMSO-d_6, 75 MHz, 300 K)



Peak Results

	Peak 1
Masses	
Calculated Mass (µg)	158.42
Molar mass moments (g/mol)	
Mn	1.426×10^4 (±6.896%)
Mw	2.725×10^4 (±6.896%)
Mz	4.452×10^4 (±15.420%)
M(avg)	4.328×10^3 (±0.324%)
Polydispersity	
Mw/Mn	1.911 (±9.752%)
Mz/Mn	3.123 (±16.892%)

Figure S22. GPC curve and data of **PPeMPS** (40°C, THF, PS as standard)

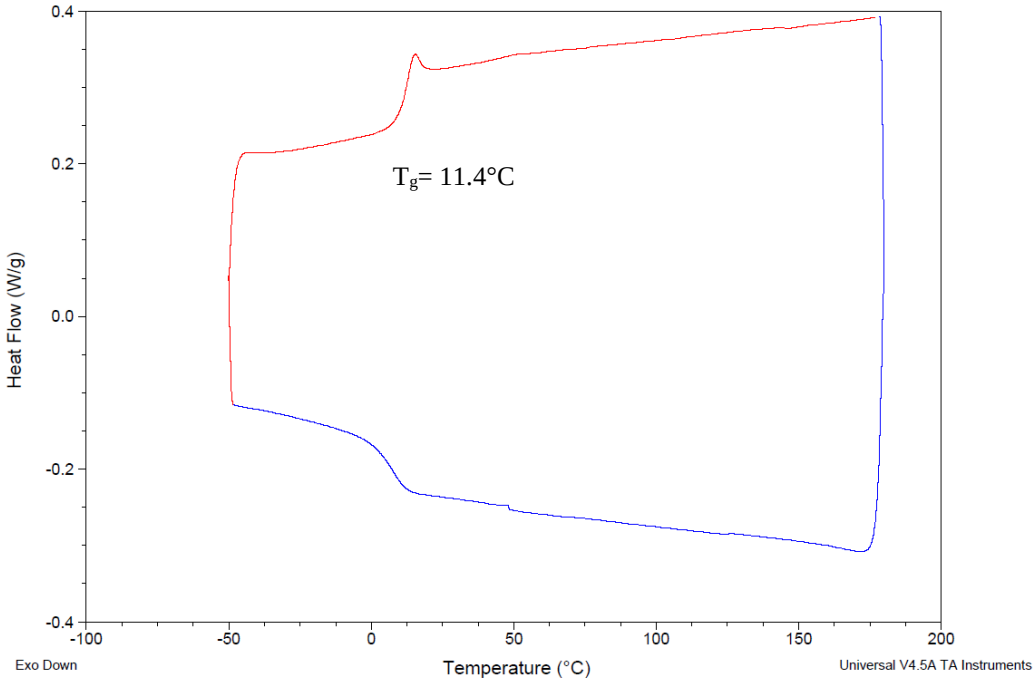


Figure S23. Second heating and cool down DSC curve of **PPeMPS** (10°C/min, exo down)

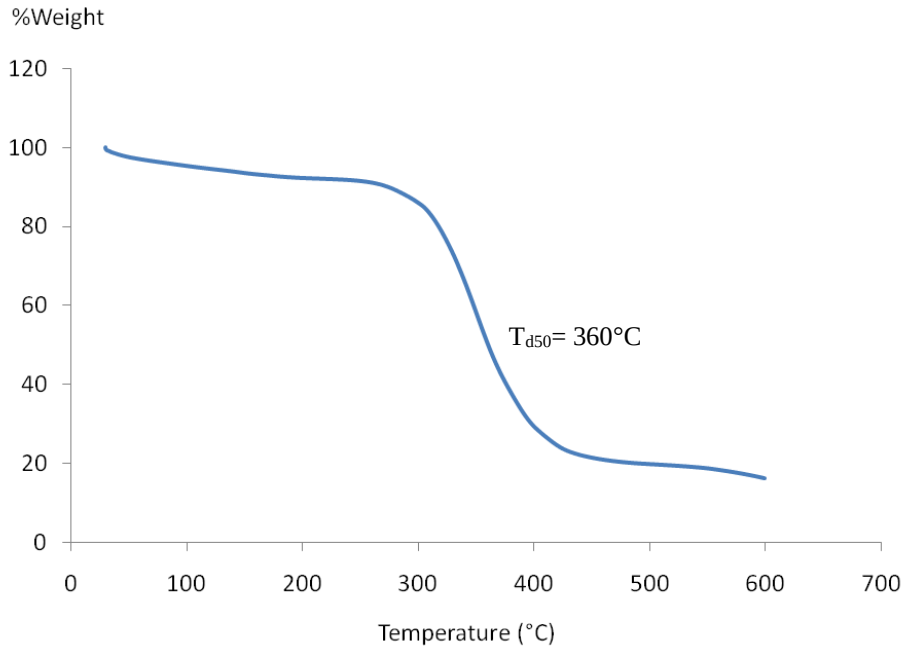


Figure S24. ATG curve of **PPeMPS** (10°C/min, under N_2)

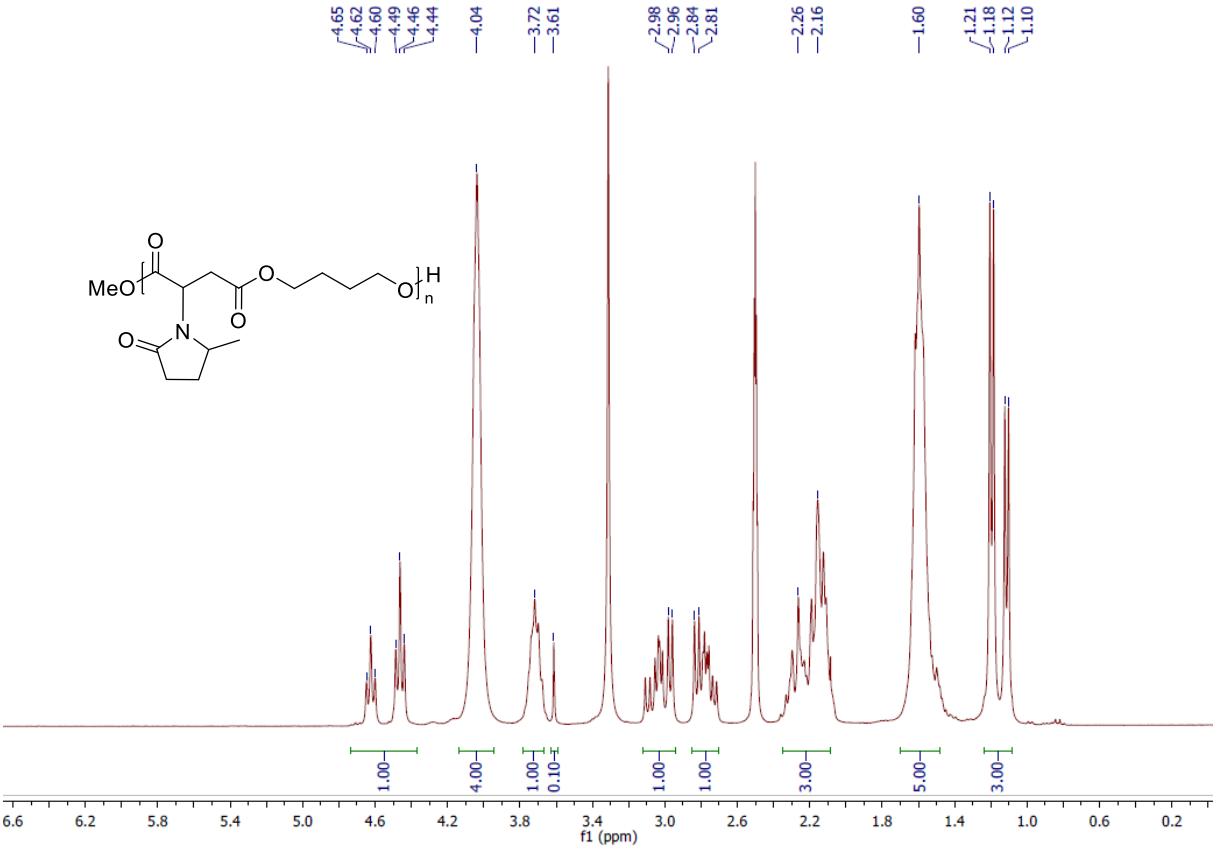


Figure S25. ^{1}H NMR Spectrum of **PBMPS** (DMSO-d_6, 300 MHz, 300 K)

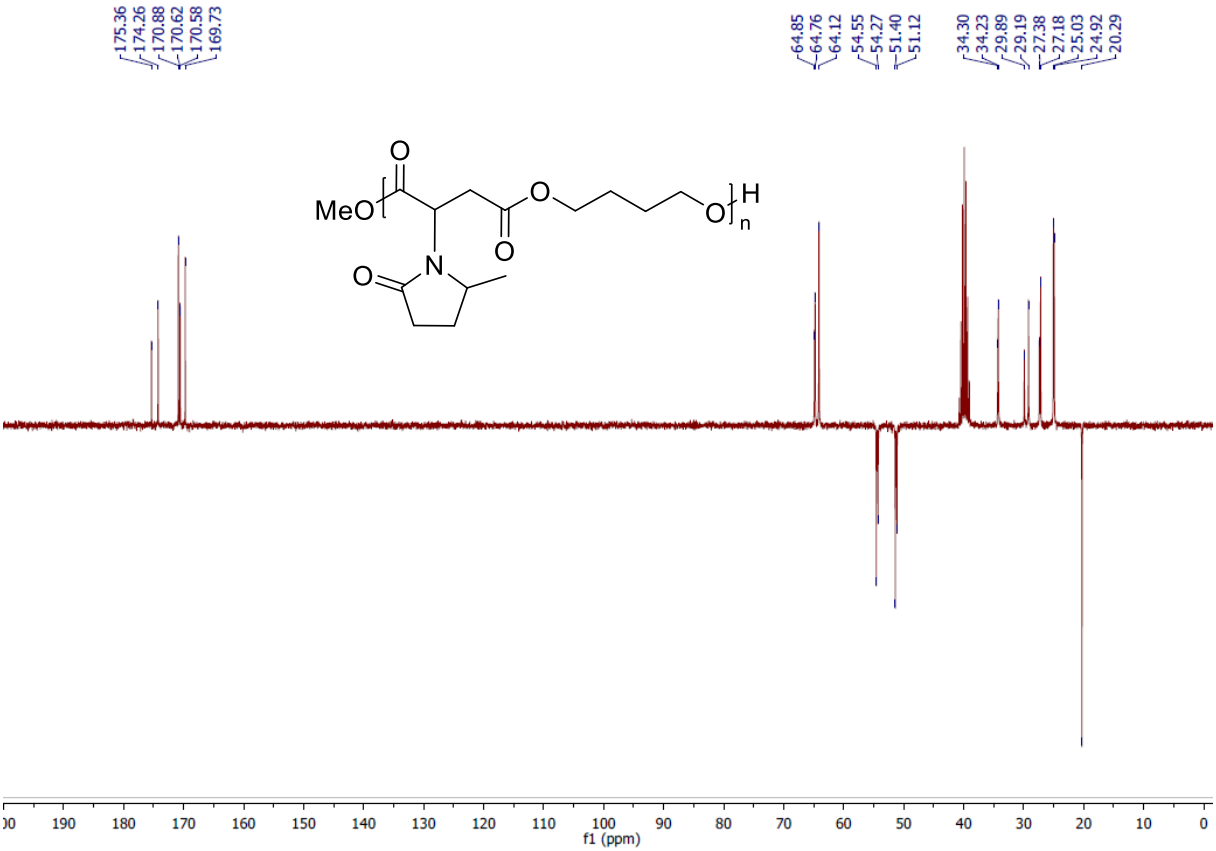
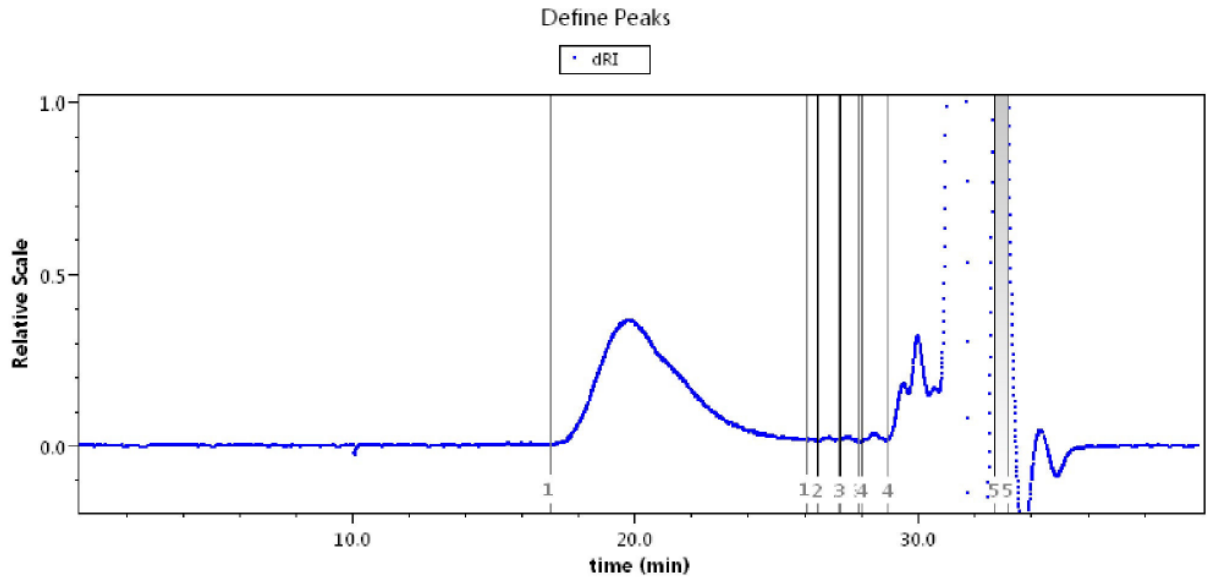


Figure S26. ^{13}C NMR Spectrum of **PBMPS** (DMSO-d_6, 75 MHz, 300 K)



Peak Results	Peak 1
Masses	
Calculated Mass (µg)	115.12
Molar mass moments (g/mol)	
Mn	9.820×10^{3} (±6.896%)
Mw	2.000×10^{4} (±6.896%)
Mz	3.262×10^{4} (±15.420%)
M(avg)	2.345×10^{3} (±0.310%)
Polydispersity	
Mw/Mn	2.037 (±9.752%)
Mz/Mn	3.321 (±16.892%)

Figure S27. GPC curve and data of **PBMPS** (40°C, THF, PS as standard)

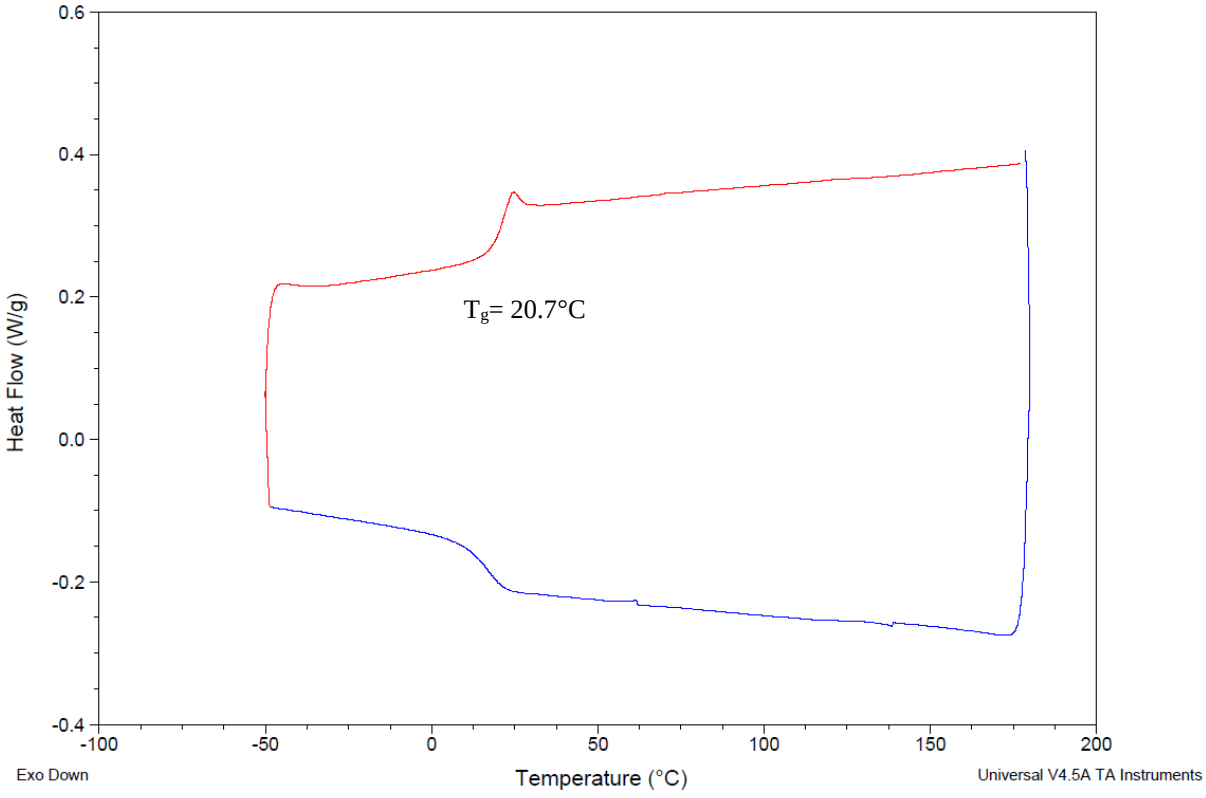


Figure S28. Second heating and cool down DSC curve of **PBMPS** (10°C/min, exo down)

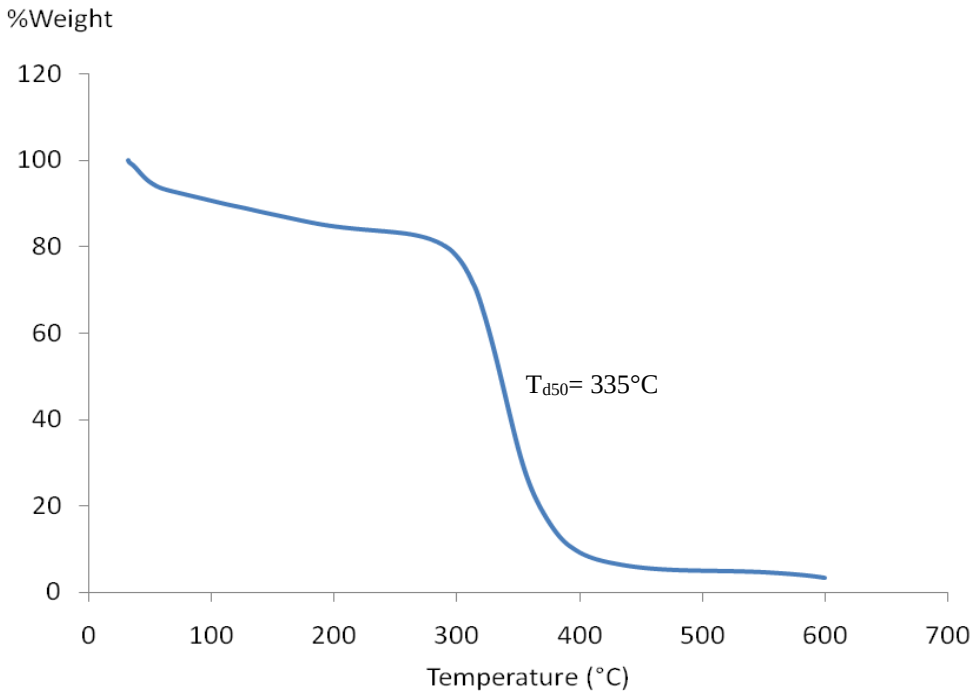


Figure S29. ATG curve of **PBMPS** (10°C/min, under N_2)

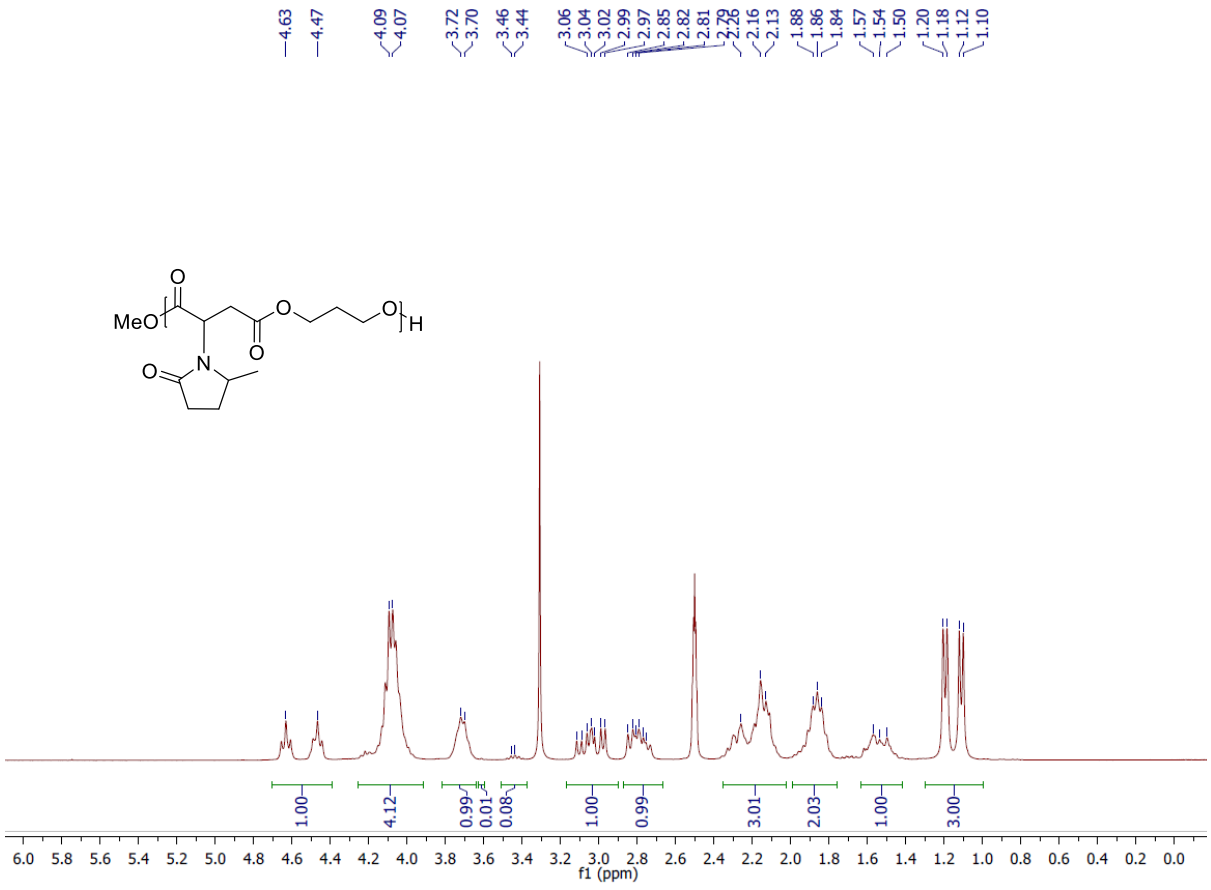


Figure S30. ^{1}H NMR Spectrum of **PPMPS** (DMSO-d_6, 300 MHz, 300 K)

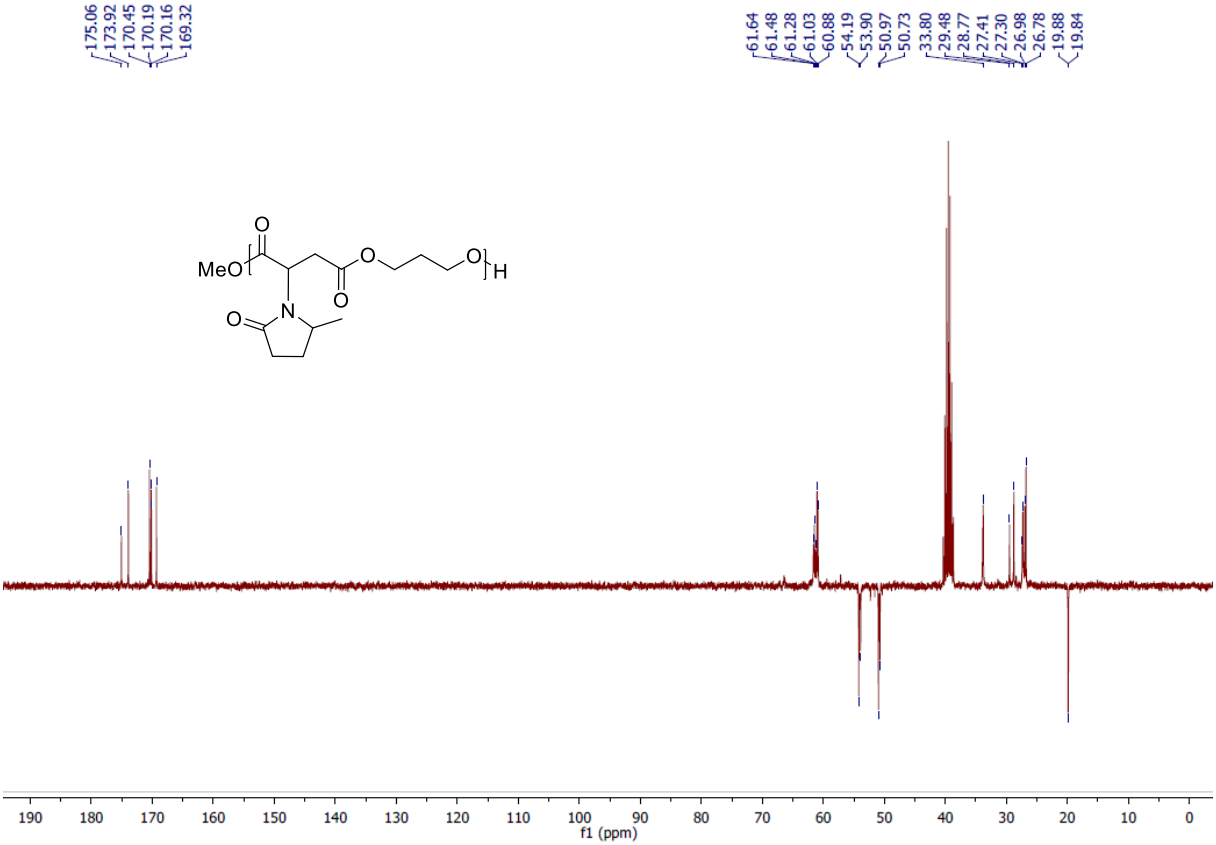
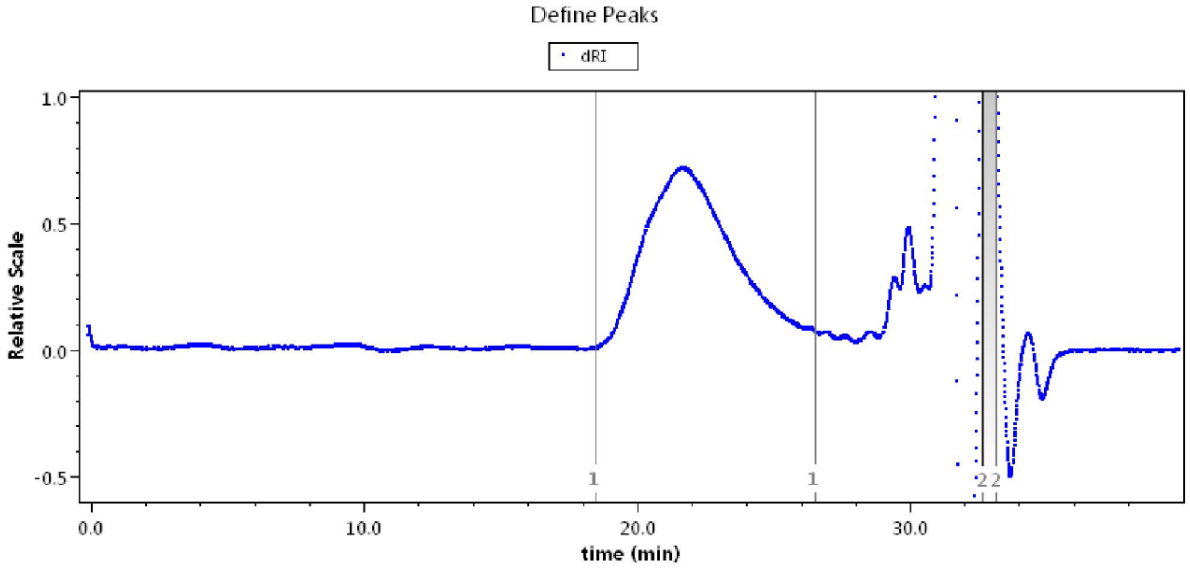


Figure S31. ^{13}C NMR Spectrum of **PPMPS** (DMSO-d_6, 75 MHz, 300 K)



Masses

Calculated Mass (µg)	171.04

Molar mass moments (g/mol)

Mn	4.925×10^{3} (±6.896%)
Mw	8.451×10^{3} (±6.896%)
Mz	1.303×10^{4} (±15.420%)
M(avg)	1.899×10^{3} (±0.310%)

Polydispersity

Mw/Mn	1.716 (±9.752%)
Mz/Mn	2.646 (±16.892%)

Figure S32. GPC curve and data of **PPMPS** (40°C, THF, PS as standard)

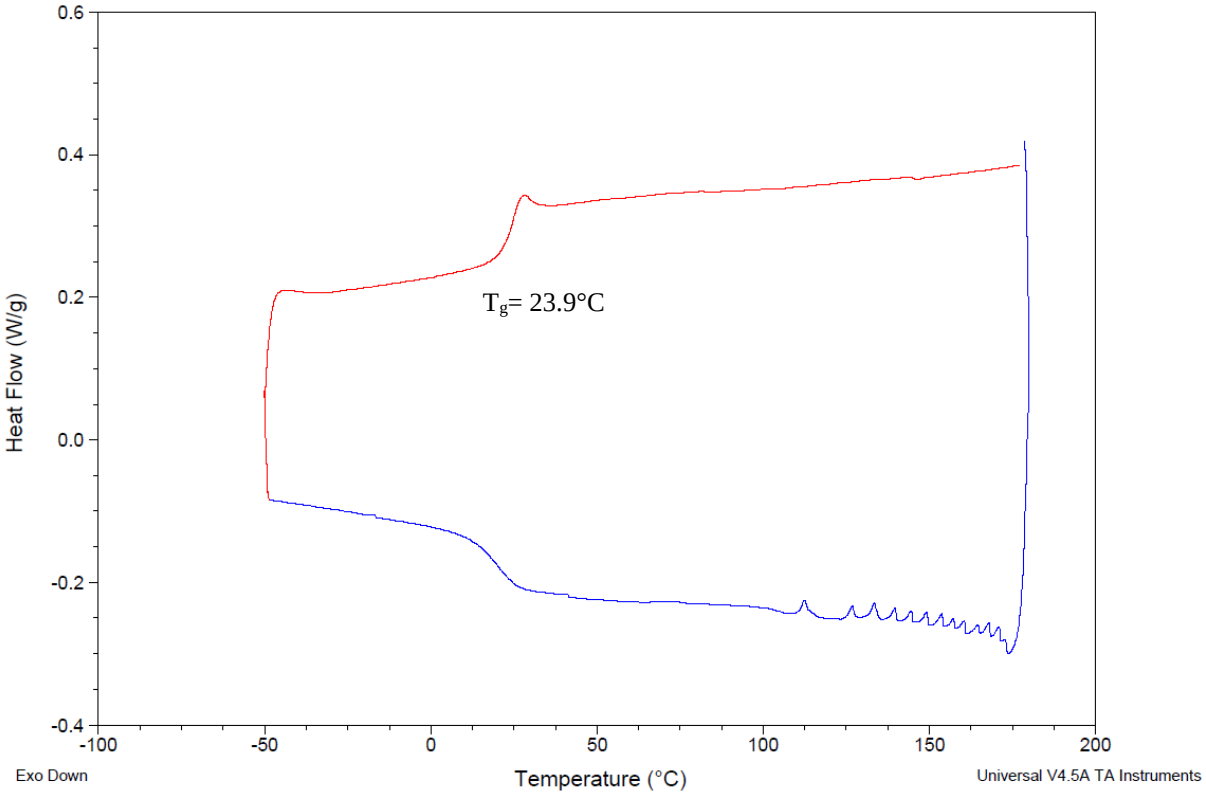


Figure S33. Second heating and cool down DSC curve of **PPMPS** (10°C/min, exo down)

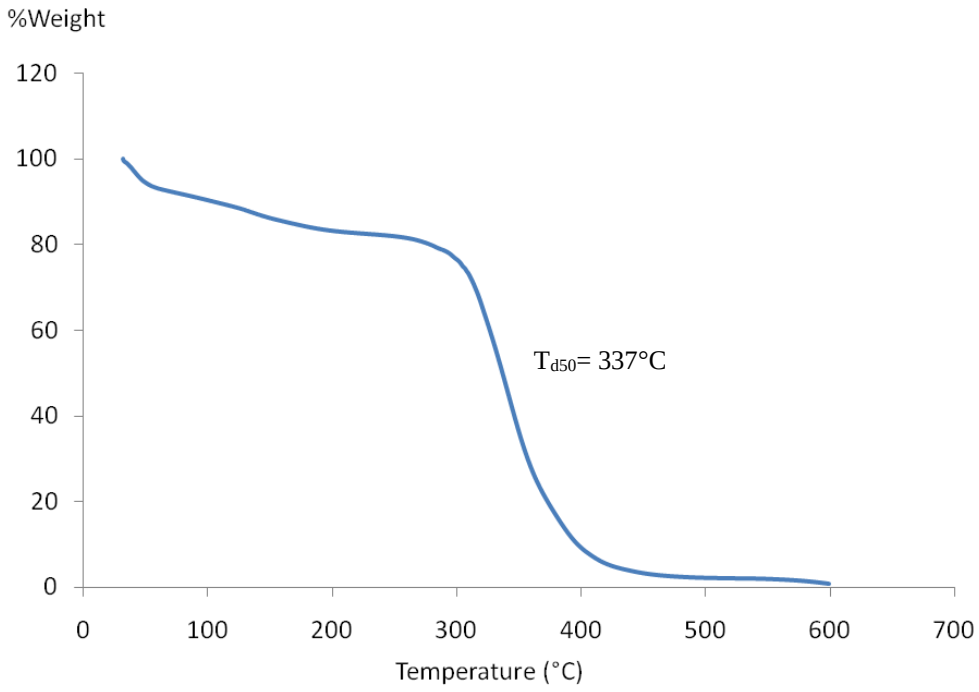


Figure S34. ATG curve of **PPMPS** (10°C/min, under N_2)

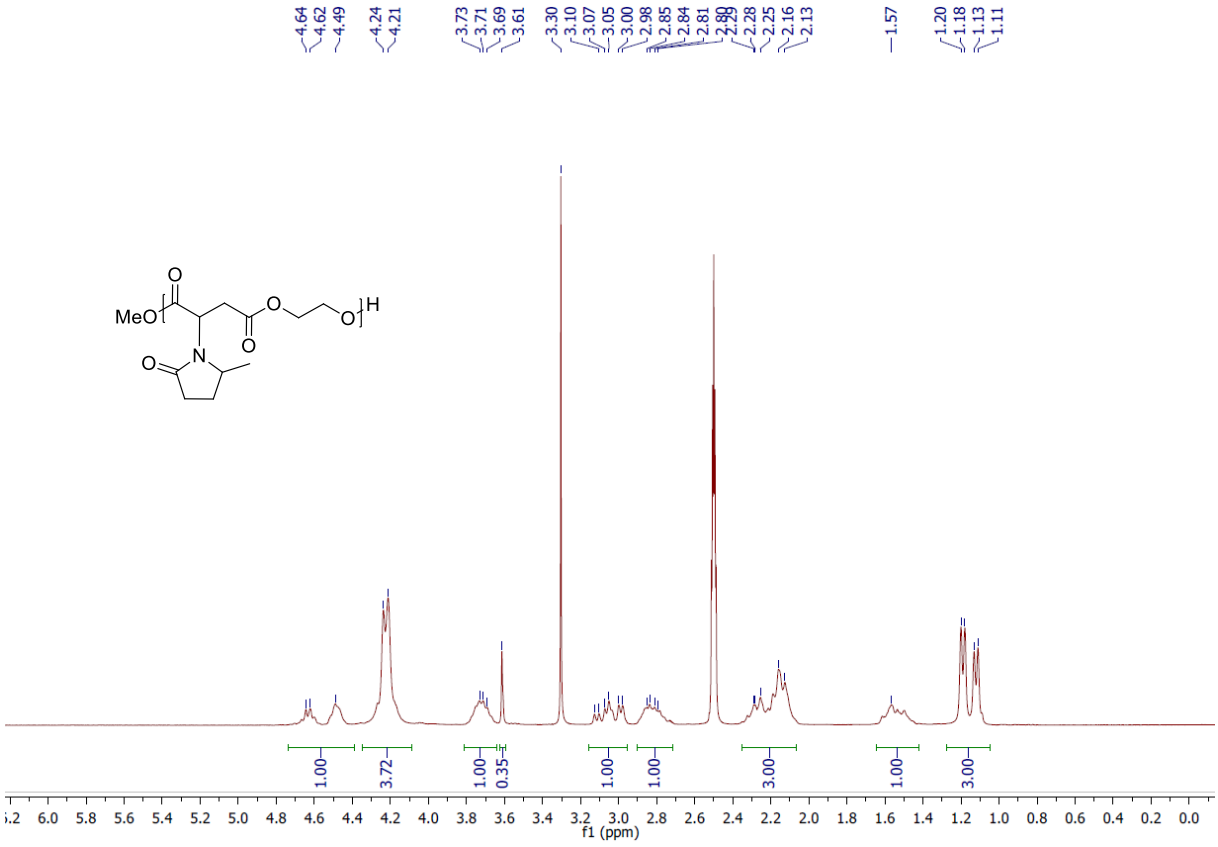


Figure S35. ^{1}H NMR Spectrum of **PEMPS** (DMSO-d_6, 300 MHz, 300 K)

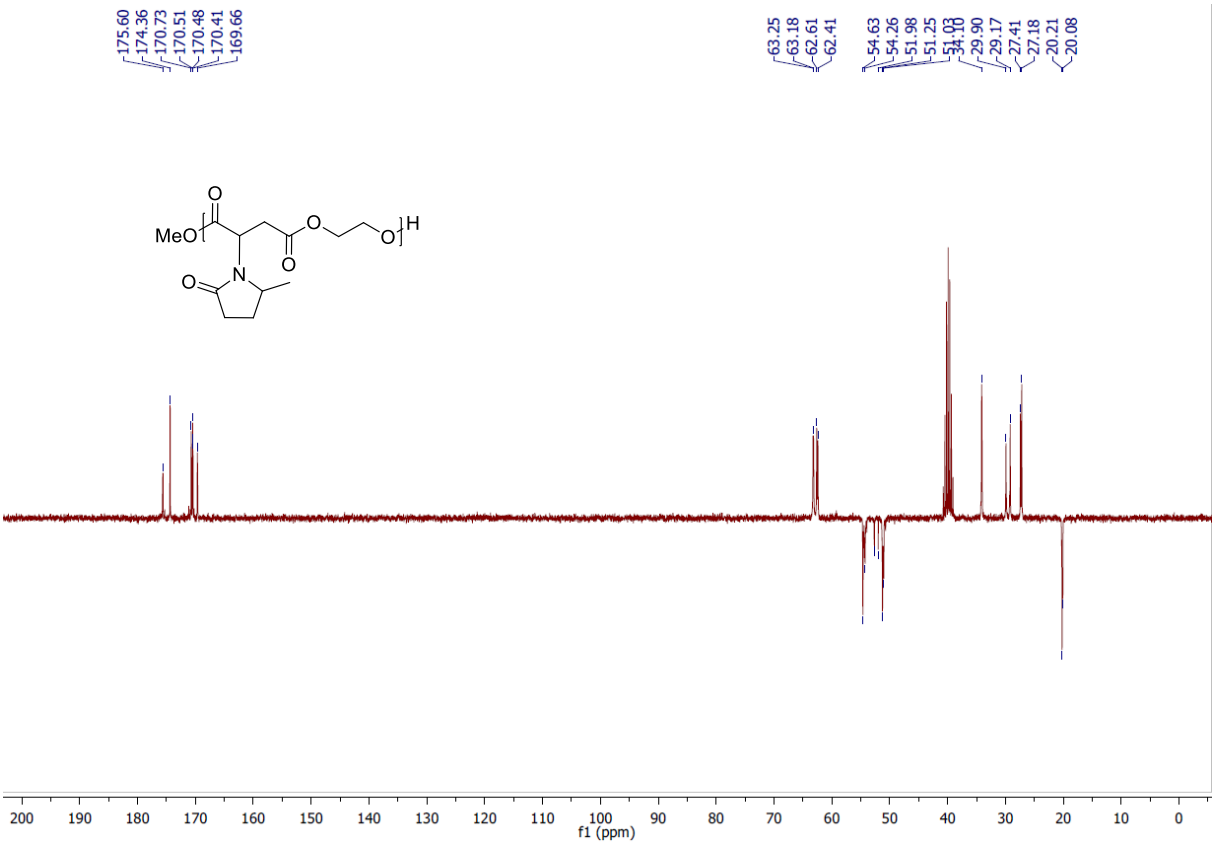
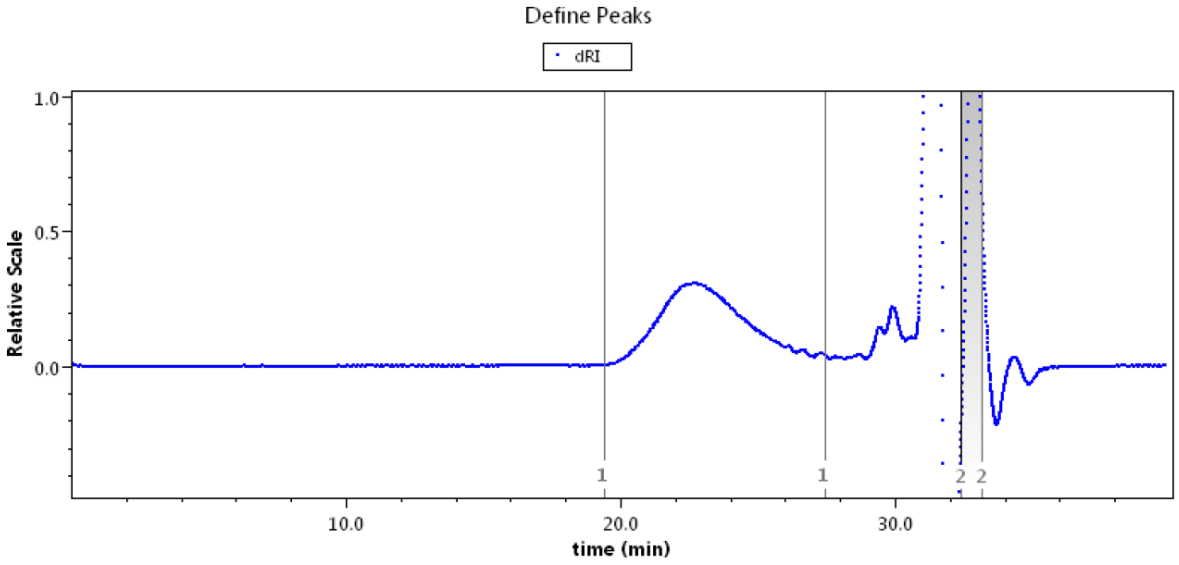


Figure S36. ^{13}C NMR Spectrum of **PEMPS** (DMSO-d_6, 75 MHz, 300 K)



Peak Results

	Peak 1
Masses	
Calculated Mass (µg)	171.94
Molar mass moments (g/mol)	
Mn	3.112×10^3 (±6.896%)
Mw	4.995×10^3 (±6.896%)
Mz	7.328×10^3 (±15.420%)
M(avg)	1.307×10^3 (±0.307%)
Polydispersity	
Mw/Mn	1.605 (±9.752%)
Mz/Mn	2.355 (±16.892%)

Figure S37. GPC curve and data of **PEMPS** (40°C, THF, PS as standard)

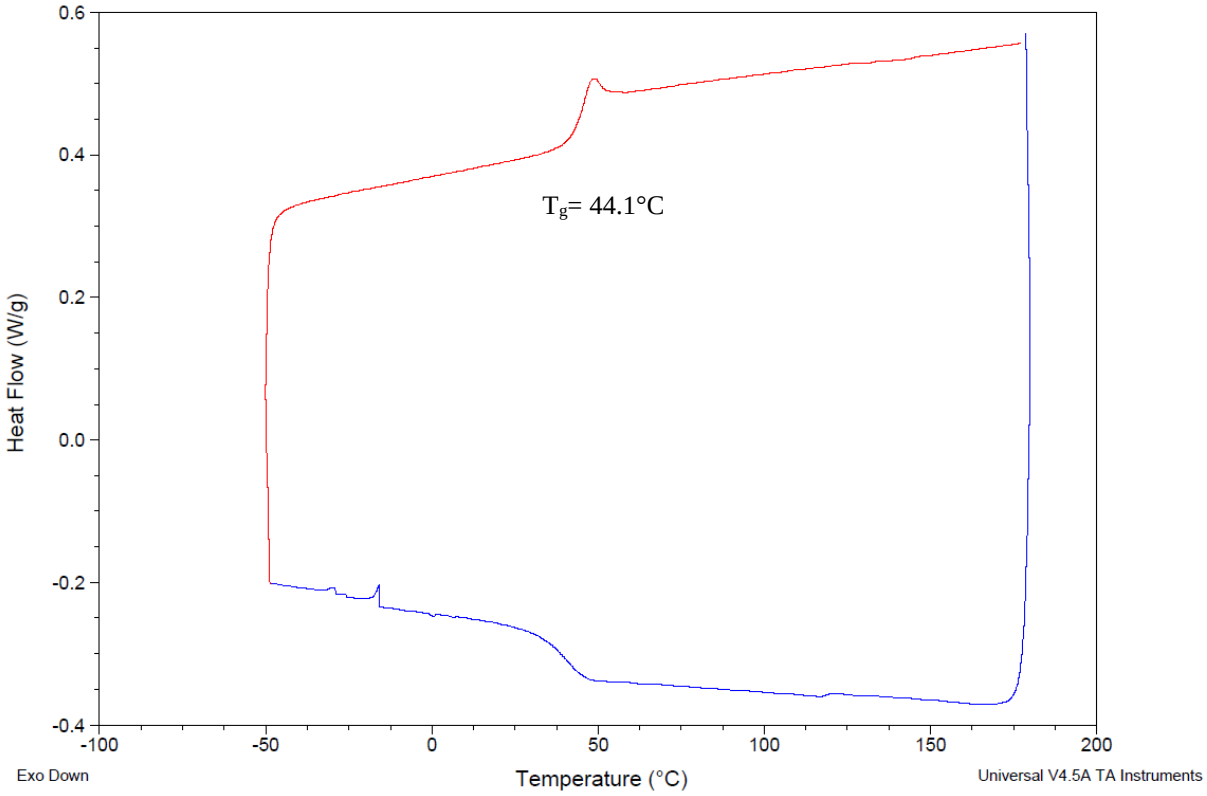


Figure S38. Second heating and cool down DSC curve of **PEMPS** (10°C/min, exo down)

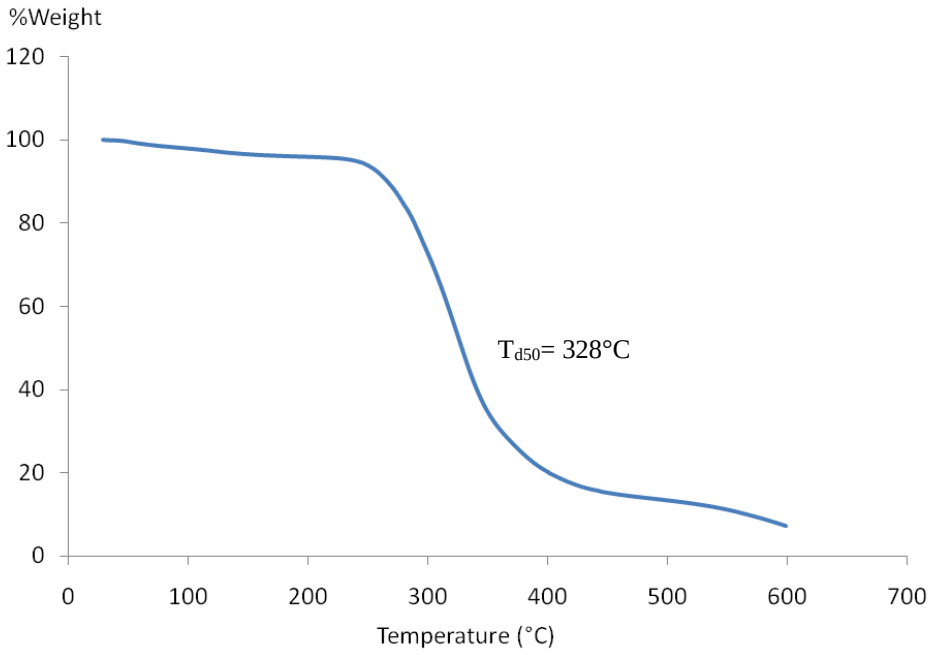


Figure S39. ATG curve of **PEMPS** (10°C/min, under N_2)