Cyclic and Spirocyclic Polyacetal Ethers from Lignin-Based Aromatics

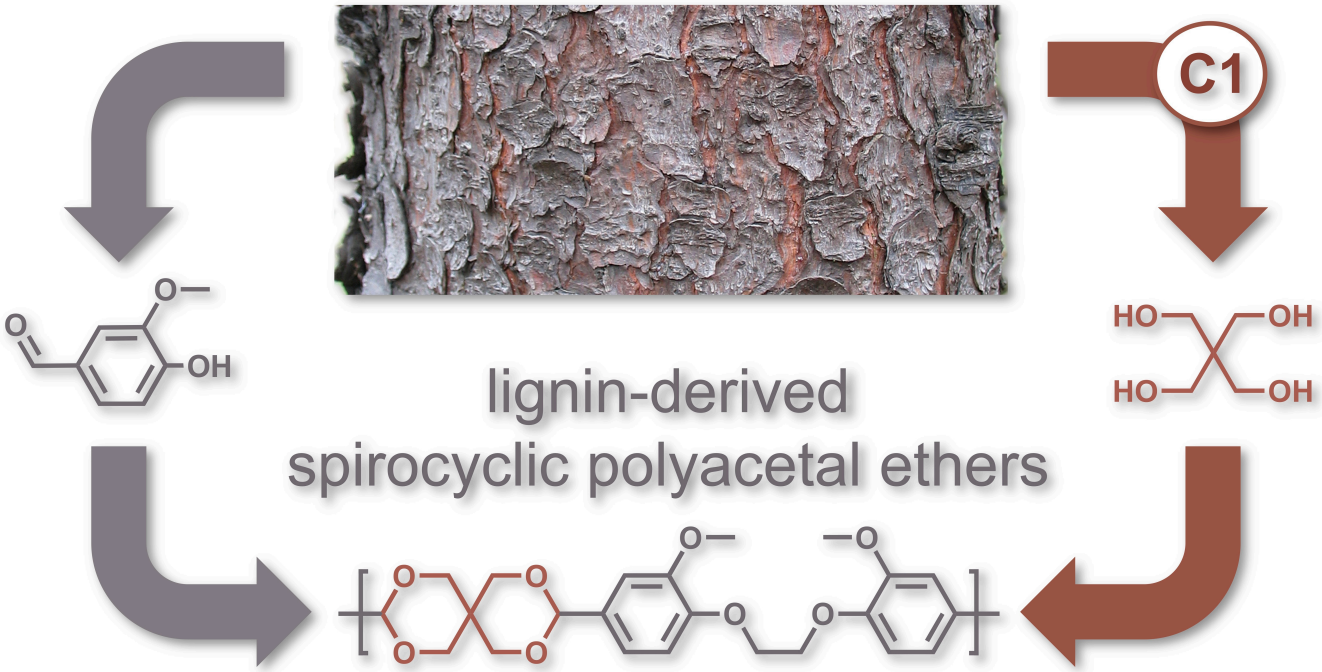
*Alexander G. Pemba, Mayra Rostagno, Tanner A. Lee and Stephen A. Miller**

The George and Josephine Butler Polymer Research Laboratory, Department of Chemistry, University of Florida Gainesville, Florida 32611-7200, USA

Electronic Supplementary Information (ESI)

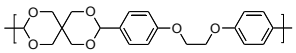
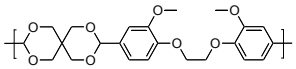
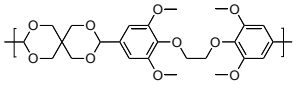
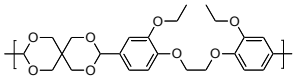
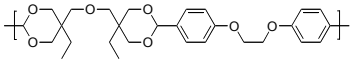
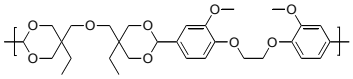
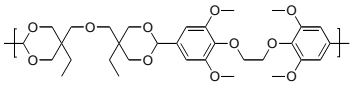
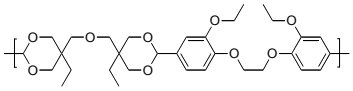
Supplementary Information Available: Complete polymer characterization data.

Table of Contents



Summary of Polymerization Data

Table S1. Thermal and molecular weight data for spirocyclic (1–4) and cyclic (5–8) polyacetal ethers.[a]

Entry	Polymer	Yield (%)	M_w (Da)	M_n (Da)	PDI	T_g (°C)	T_m (°C)	T_{95} (°C)[d]	Residue (%)[d]
1[b] **P-BB**		81	[c]	[c]	[c]	*n.o.*	*n.o.*	328	20
2 **P-VV**		90	23,700	10,600	2.2	129	*n.o.*	308	19
3 **P-SS**		90	36,000	18,600	1.9	152	*n.o.*	307	17
4 **P-EE**		83	47,800	18,500	2.6	108	*n.o.*	326	23
5 **D-BB**		81	3,500	2,600[e]	1.4	*n.o.*	259	349	8.3
6 **D-VV**		90	44,200	22,200	2.0	80	*n.o.*	327	8.2
7 **D-SS**		90	34,600	21,600	1.6	98	*n.o.*	320	12
8 **D-EE**		83	42,100	19,300	2.2	68	*n.o.*	333	10

[a]Polymerization conducted in refluxing methylene chloride at 40 °C, except as noted. Molecular weight data obtained by GPC in hexafluoroisopropanol (HFIP) solvent. For DSC data, *n.o.* indicates a thermal transition not observed. [b]Polymerization conducted in refluxing 1,1,2,2-tetrachloroethane at 146 °C. [c]Although insolubility prevented GPC analysis for **P-BB**, ^{1}H NMR spectroscopy confirmed the absence of aldehydic hydrogens characteristic of the monomer. [d]Thermogravimetric analysis conducted under nitrogen; temperature reported upon 5% mass loss; residue (%) reported at end of TGA experiment. [e]Acidity of HFIP degraded the sample before GPC analysis of **D-BB.** Nonetheless, ^{1}H NMR spectroscopy confirmed the absence of aldehydic hydrogens characteristic of the monomer.

Gel Permeation Chromatography (GPC) Analysis (in hexafluoroisopropanol, HFIP)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	22636	10601	23713	35982	49249	34180	2.237

Peak information

	Start (mins)	End (mins)
Baseline region 1	21.79	24.79
Baseline region 2	52.23	55.23
Peak 1	30.00	39.47

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	33.96	8261878.103	36693.014

Chromatogram

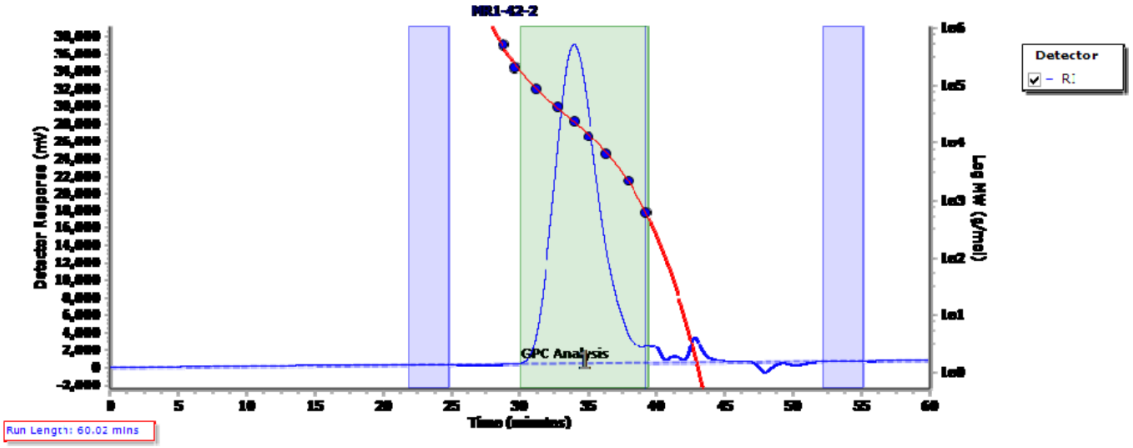


Figure S1. GPC Chromatogram of **P-VV** (Table S1, entry 2).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	34555	18579	36007	55512	80338	52399	1.938

Peak information

	Start (mins)	End (mins)
Baseline region 1	19.68	25.37
Baseline region 2	45.55	48.58
Peak 1	28.84	38.43

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	33.02	9732799.980	44984.223

Chromatogram

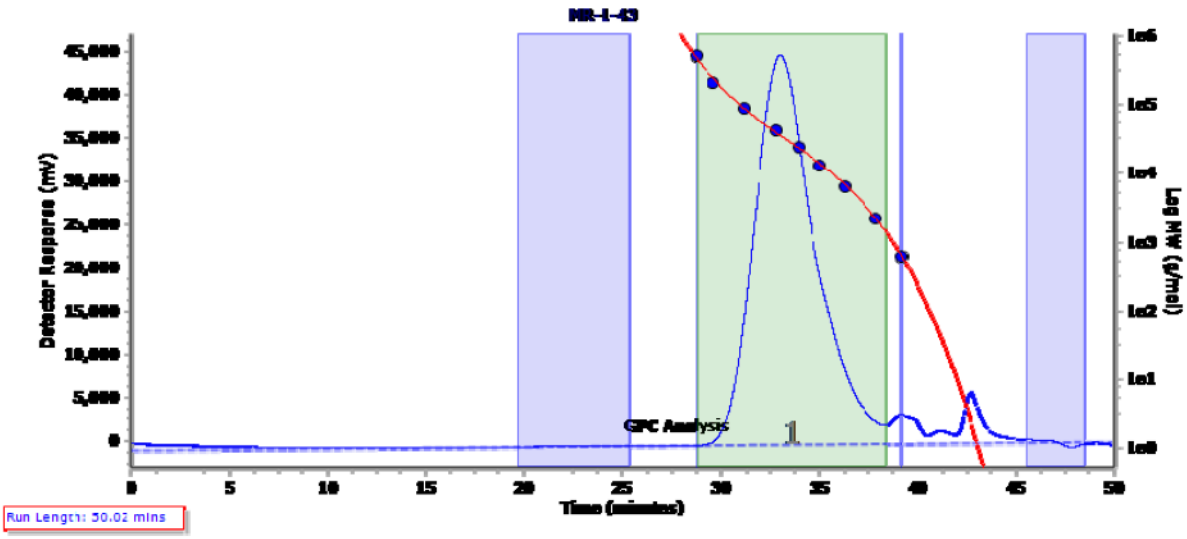


Figure S2. GPC Chromatogram of **P-SS** (Table S1, entry 3).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	40901	18469	47786	85802	141919	79217	2.587

Peak information

	Start (mins)	End (mins)
Baseline region 1	22.74	25.24
Baseline region 2	45.48	46.22
Peak 1	28.55	39.25

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	32.66	8054002.391	31880.956

Chromatogram

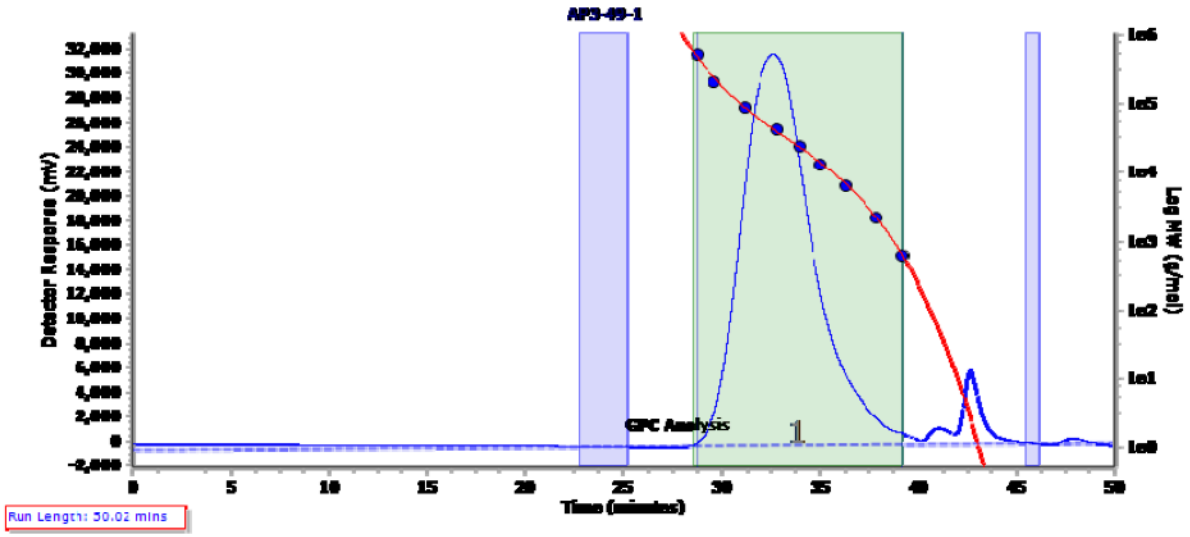


Figure S3. GPC Chromatogram of **P-EE** (Table S1, entry 4).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	2555	2569	3504	4763	6111	4567	1.364

Peak information

	Start (mins)	End (mins)
Baseline region 1	21.24	24.24
Baseline region 2	52.68	55.68
Peak 1	34.85	38.62

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	37.66	239429.903	1979.690

Chromatogram

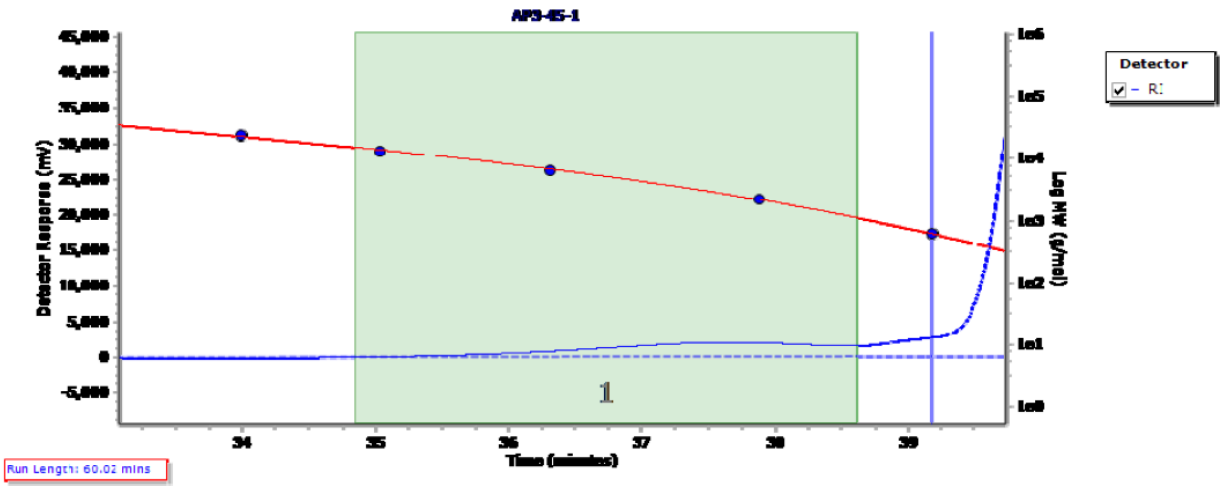


Figure S4. GPC Chromatogram of **D-BB** (Table S1, entry 5).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	34713	22246	44198	78090	129686	72046	1.987

Peak information

	Start (mins)	End (mins)
Baseline region 1	20.42	23.42
Baseline region 2	55.70	58.70
Peak 1	28.67	37.65

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	33.02	13751703.772	56737.240

Chromatogram

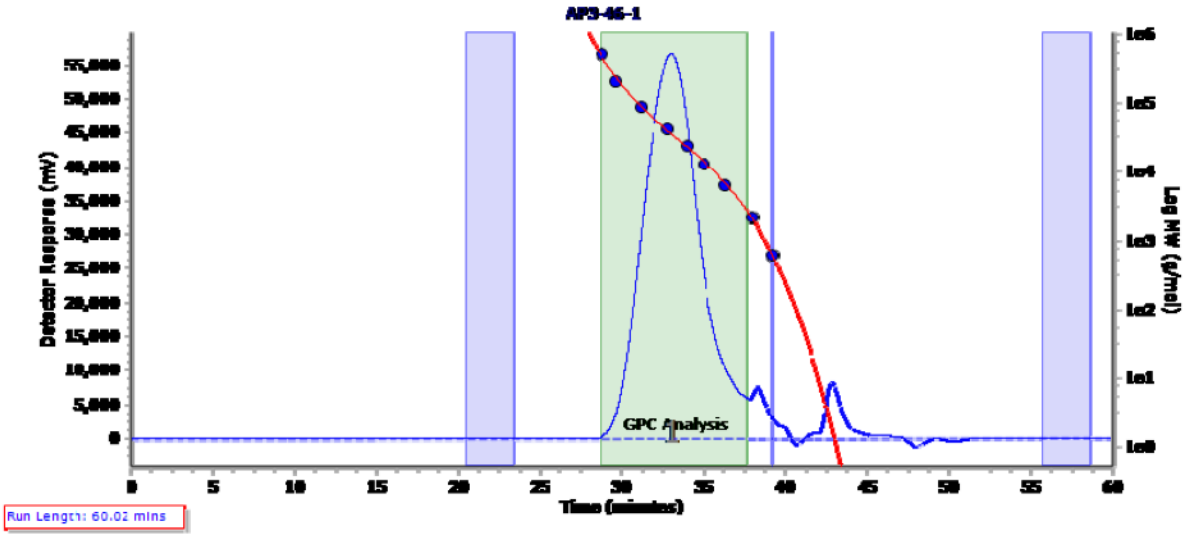


Figure S5. GPC Chromatogram of **D-VV** (Table S1, entry 6).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	28989	21590	34623	50968	71673	48305	1.604

Peak information

	Start (mins)	End (mins)
Baseline region 1	22.28	25.28
Baseline region 2	52.43	55.43
Peak 1	29.41	37.43

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	33.41	10001500.829	47844.869

Chromatogram

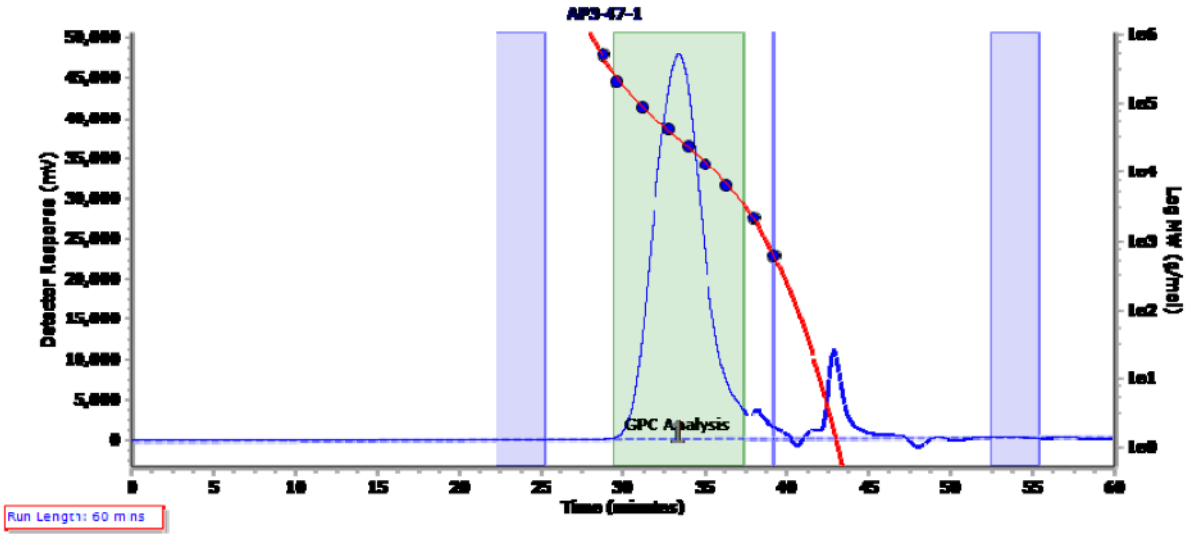


Figure S6. GPC Chromatogram of **D-SS** (Table S1, entry 7).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	36337	19263	42066	75095	124241	69396	2.184

Peak information

	Start (mins)	End (mins)
Baseline region 1	21.79	24.79
Baseline region 2	55.31	58.31
Peak 1	28.46	37.85

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	32.91	7522303.056	28981.610

Chromatogram

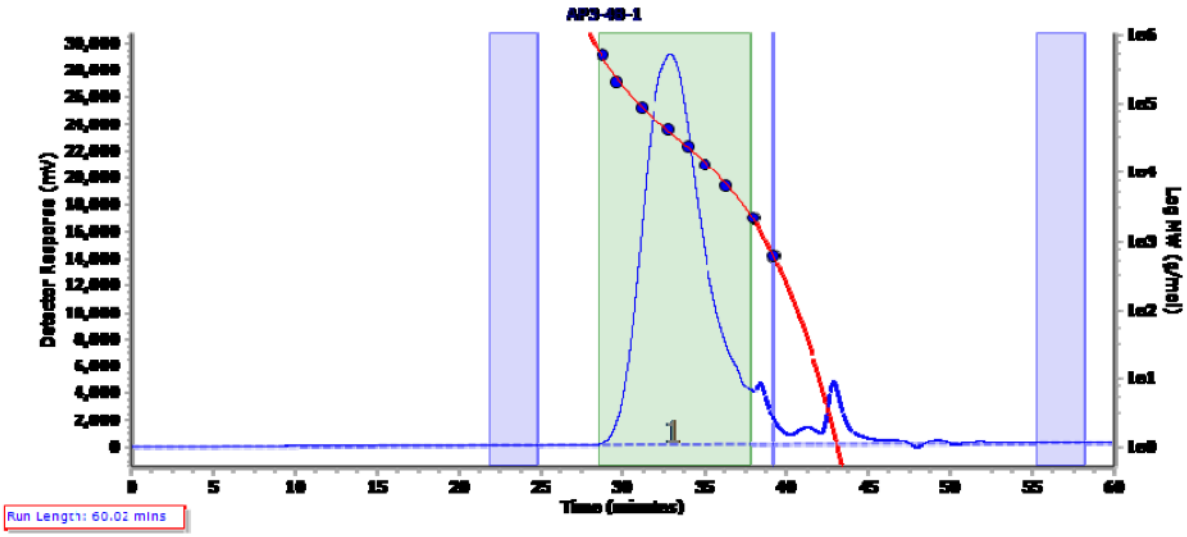


Figure S7. GPC Chromatogram of **D-EE** (Table S1, entry 8).

Differential Scanning Calorimetry (DSC) Thermograms

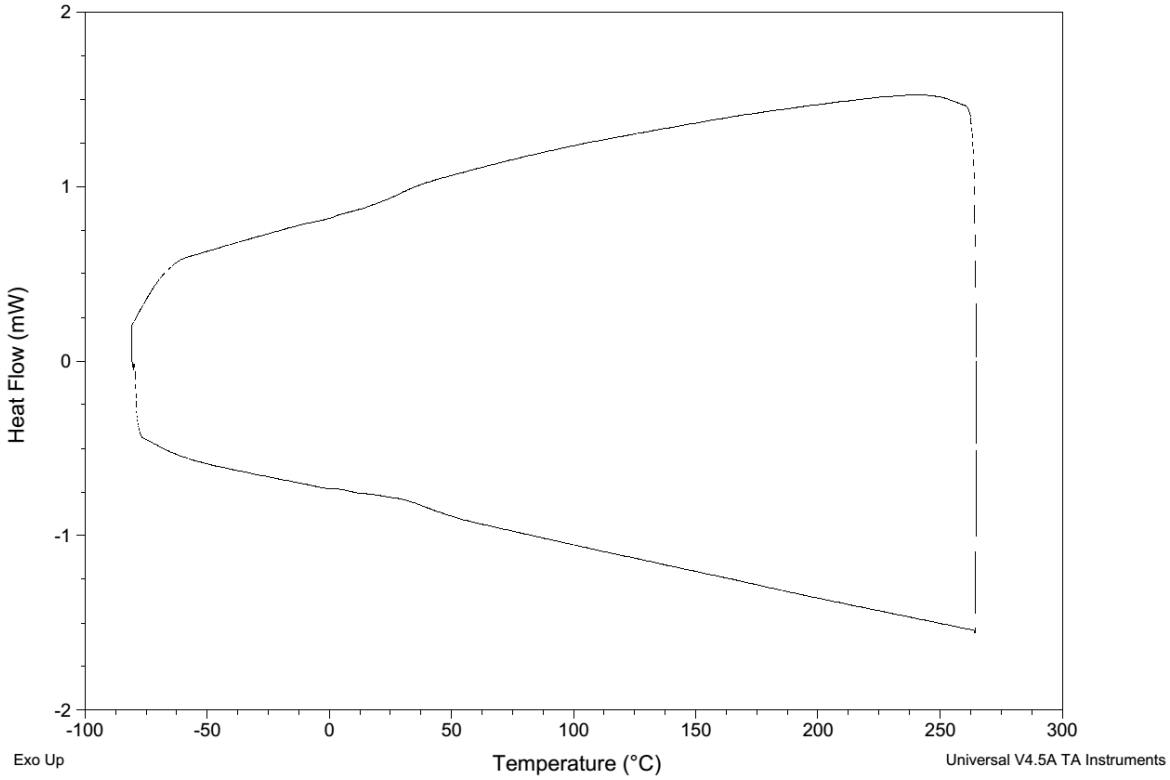


Figure S8. DSC Thermogram of **P-BB** (Table S1, entry 1).

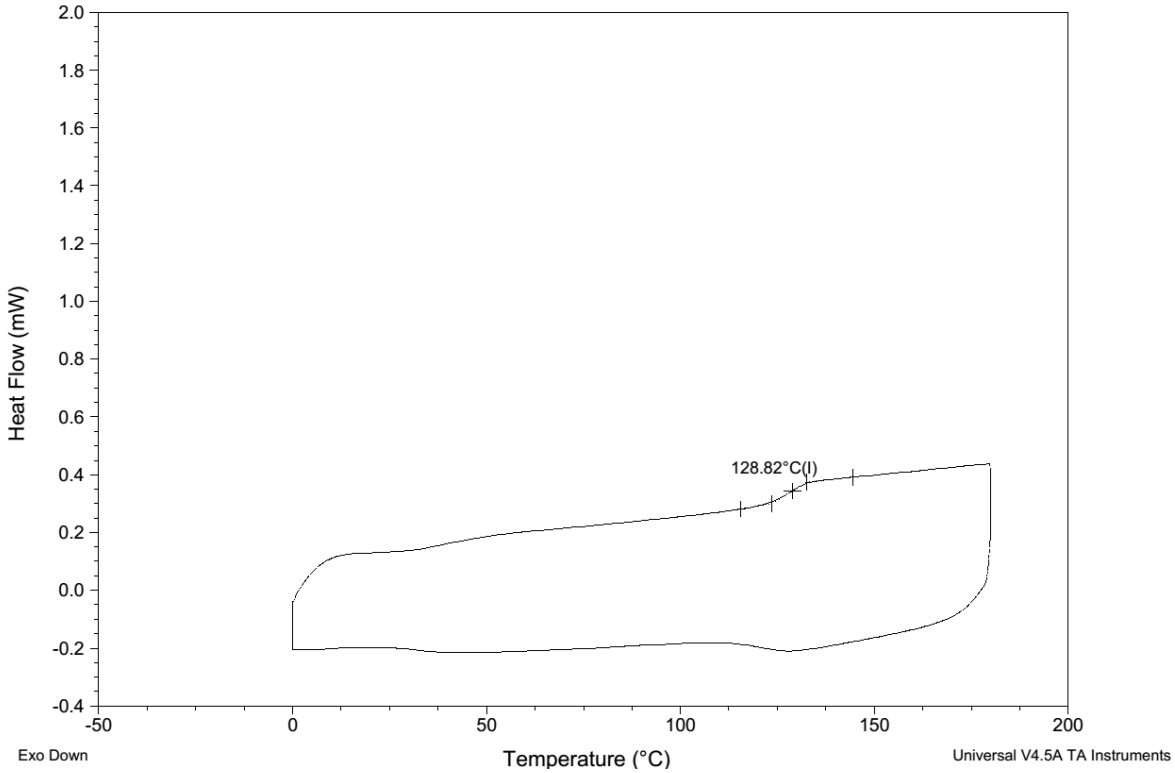


Figure S9. DSC Thermogram of **P-VV** (Table S1, entry 2).

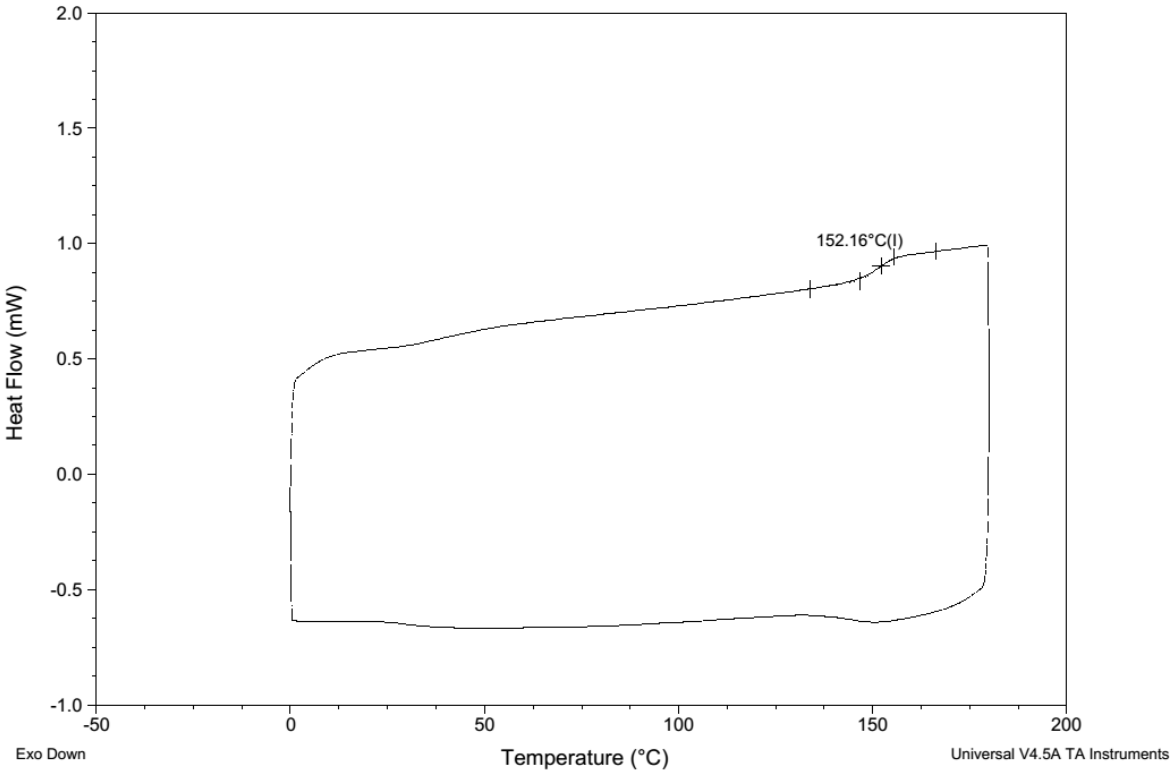


Figure S10. DSC Thermogram of **P-SS** (Table S1, entry 3).

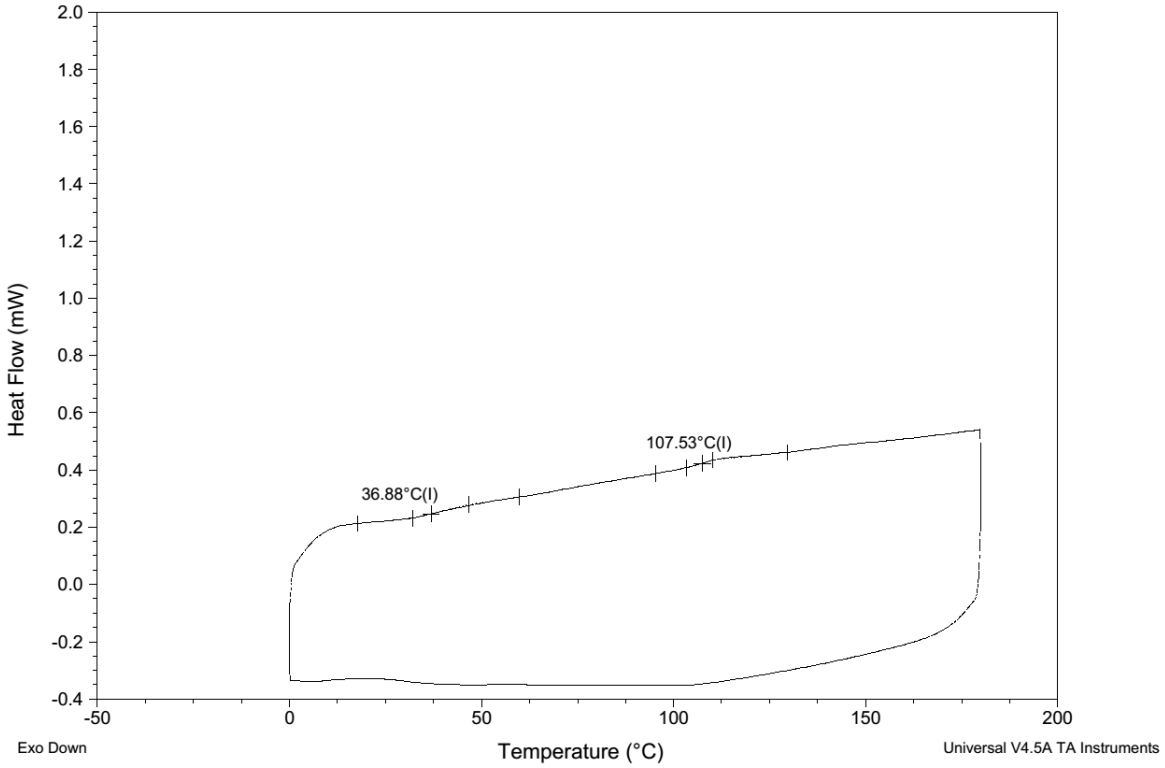


Figure S11. DSC Thermogram of **P-EE** (Table S1, entry 4).

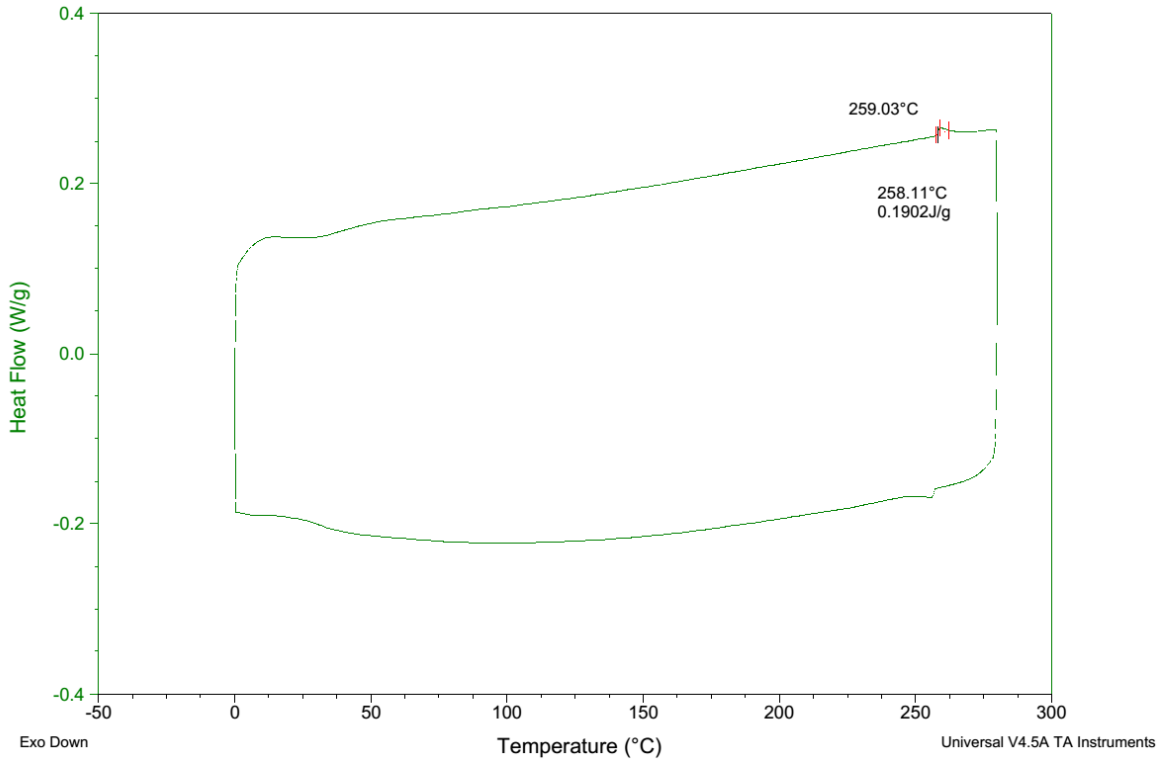


Figure S12. DSC Thermogram of **D-BB** (Table S1, entry 5).

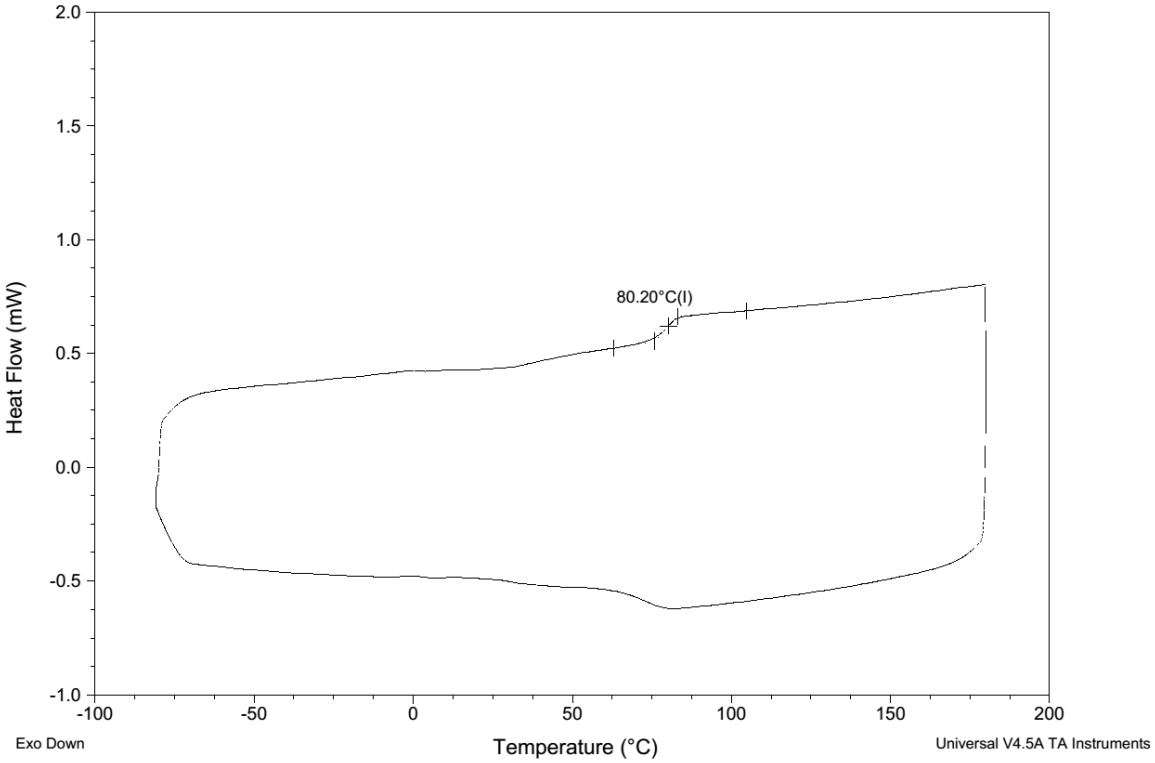


Figure S13. DSC Thermogram of **D-VV** (Table S1, entry 6).

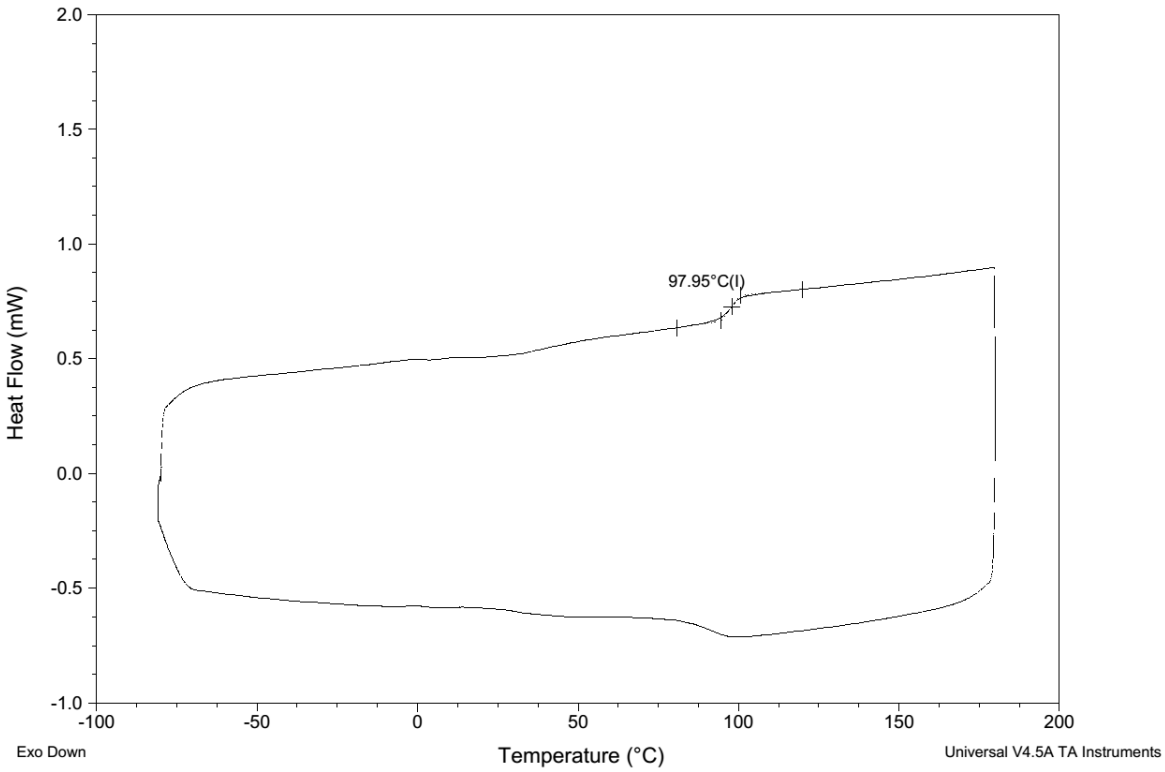


Figure S14. DSC Thermogram of **D-SS** (Table S1, entry 7).

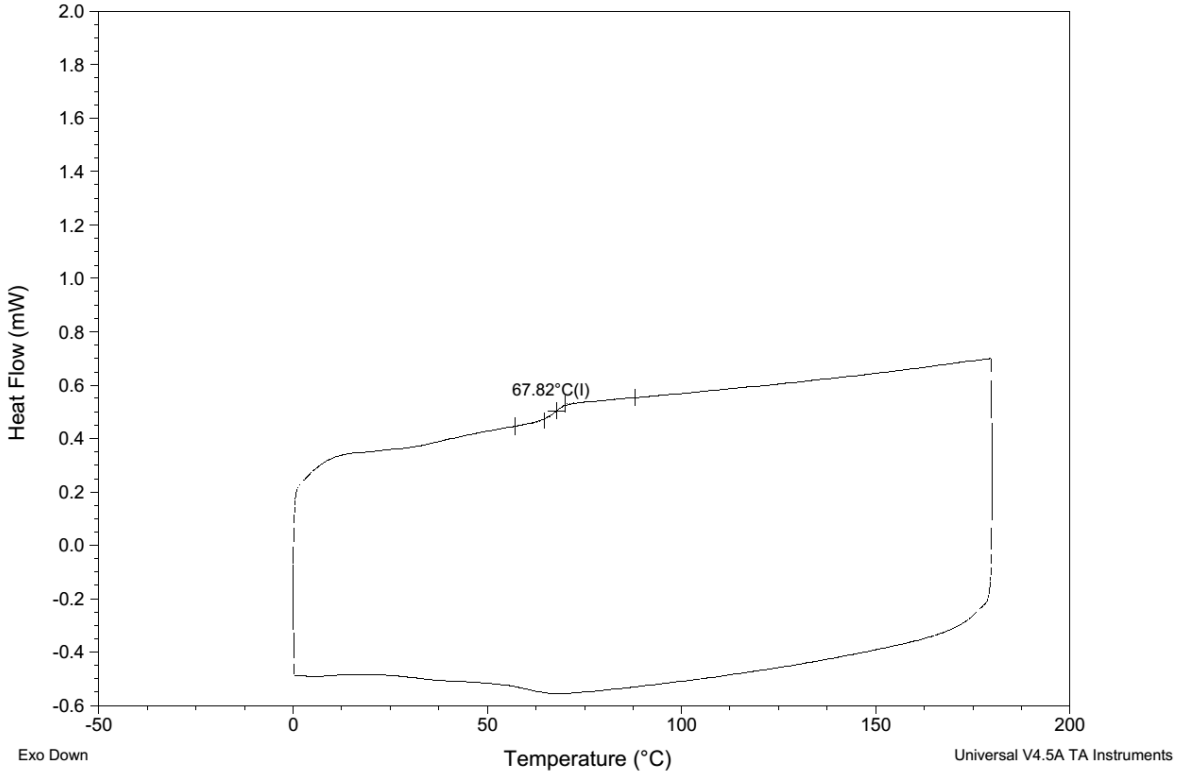


Figure S15. DSC Thermogram of **D-EE** (Table S1, entry 8).

Thermogravimetric Analysis (TGA) Thermograms

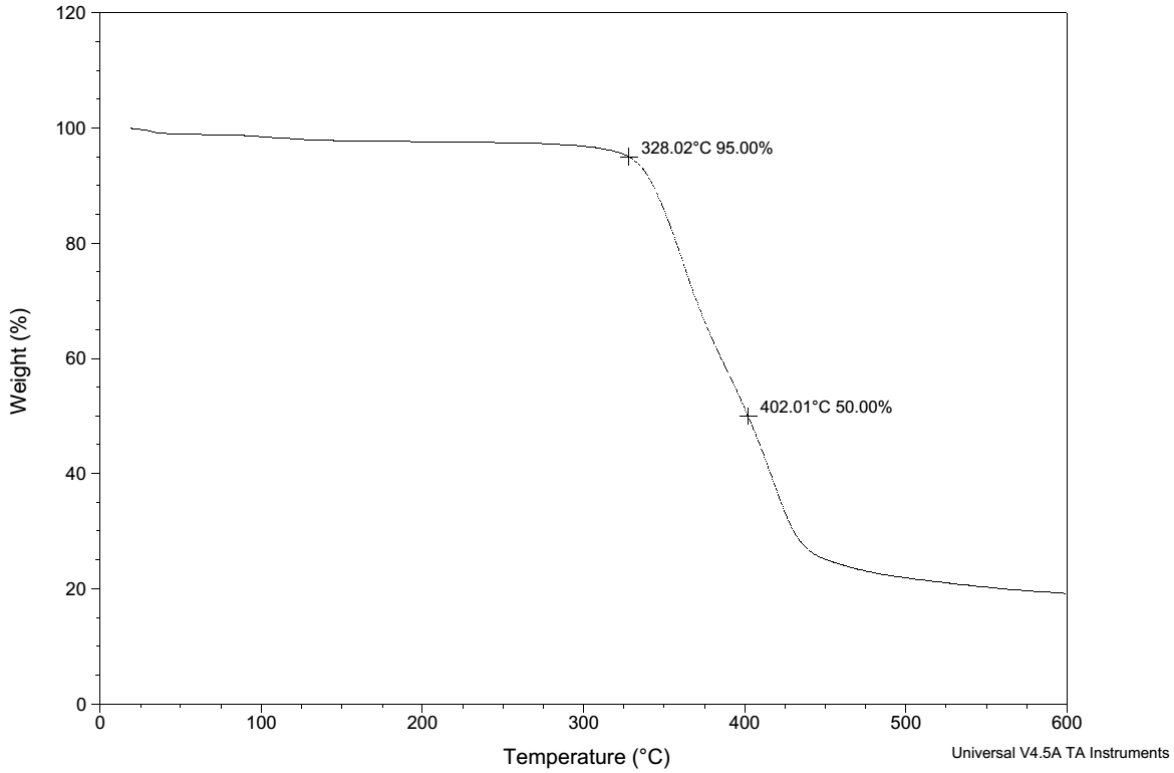


Figure S16. TGA Thermogram of **P-BB** (Table S1, entry 1).

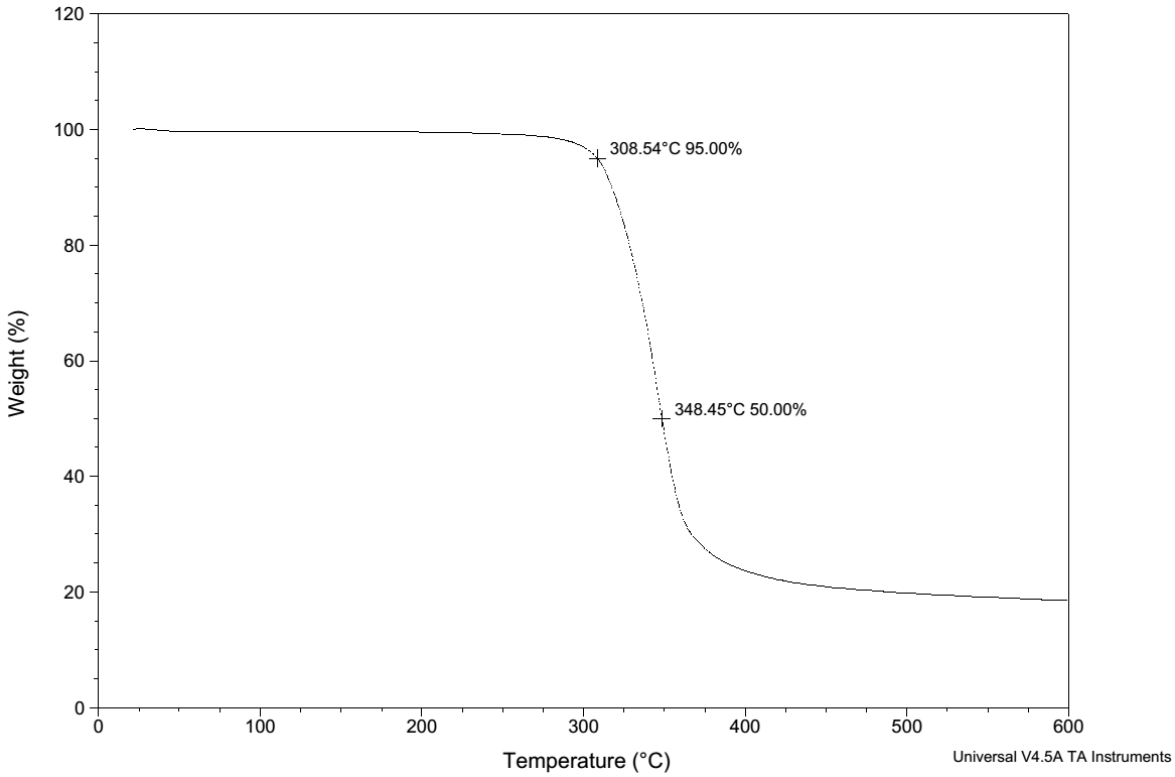


Figure S17. TGA Thermogram of **P-VV** (Table S1, entry 2).

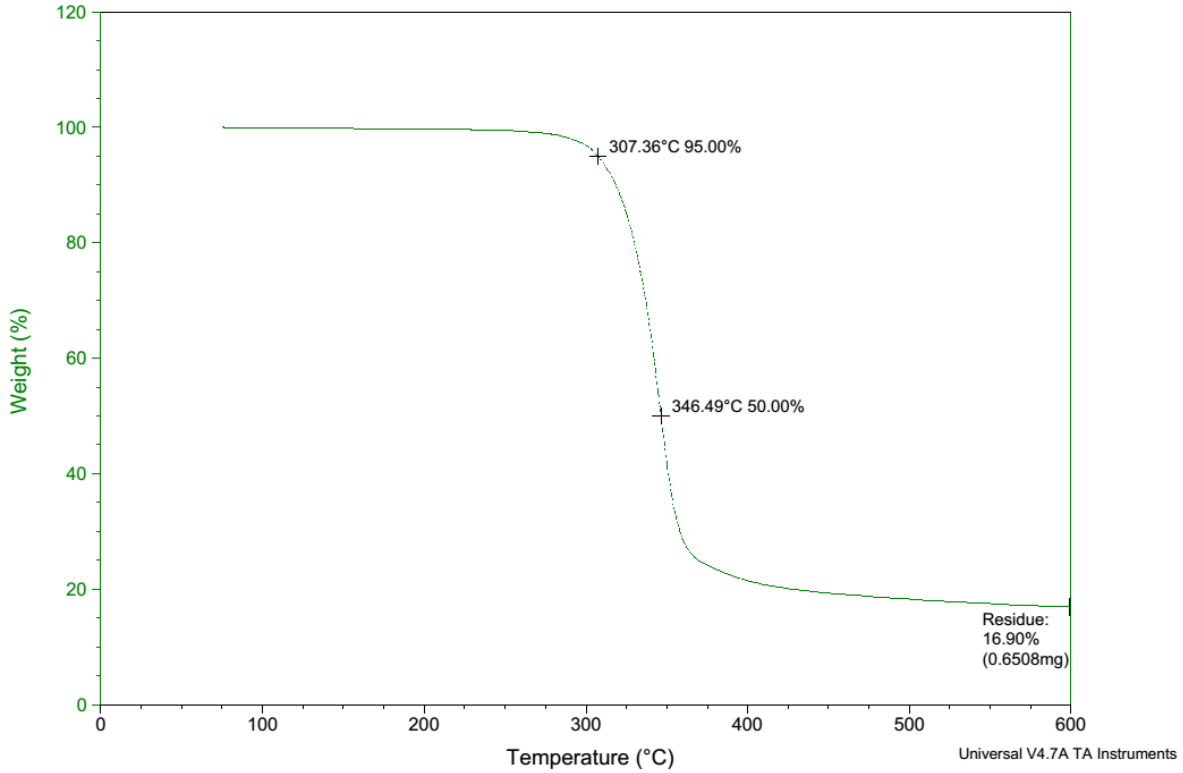


Figure S18. TGA Thermogram of **P-SS** (Table S1, entry 3).

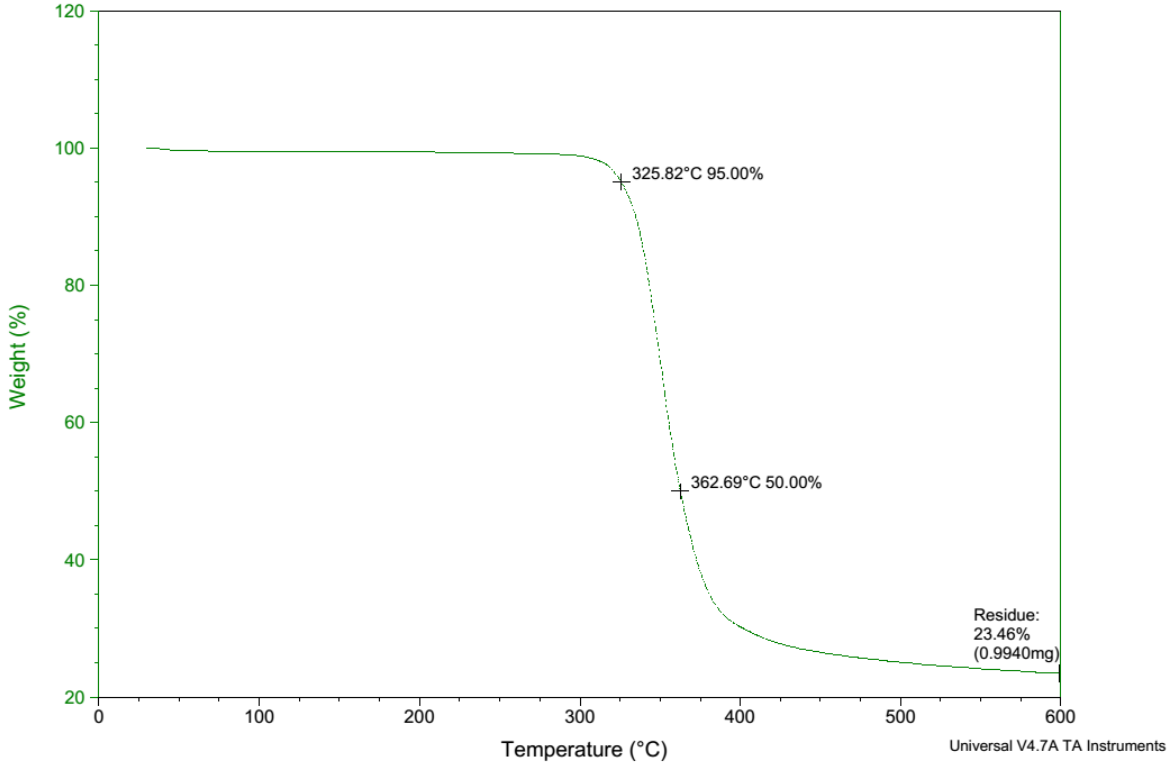


Figure S19. TGA Thermogram of **P-EE** (Table S1, entry 4).

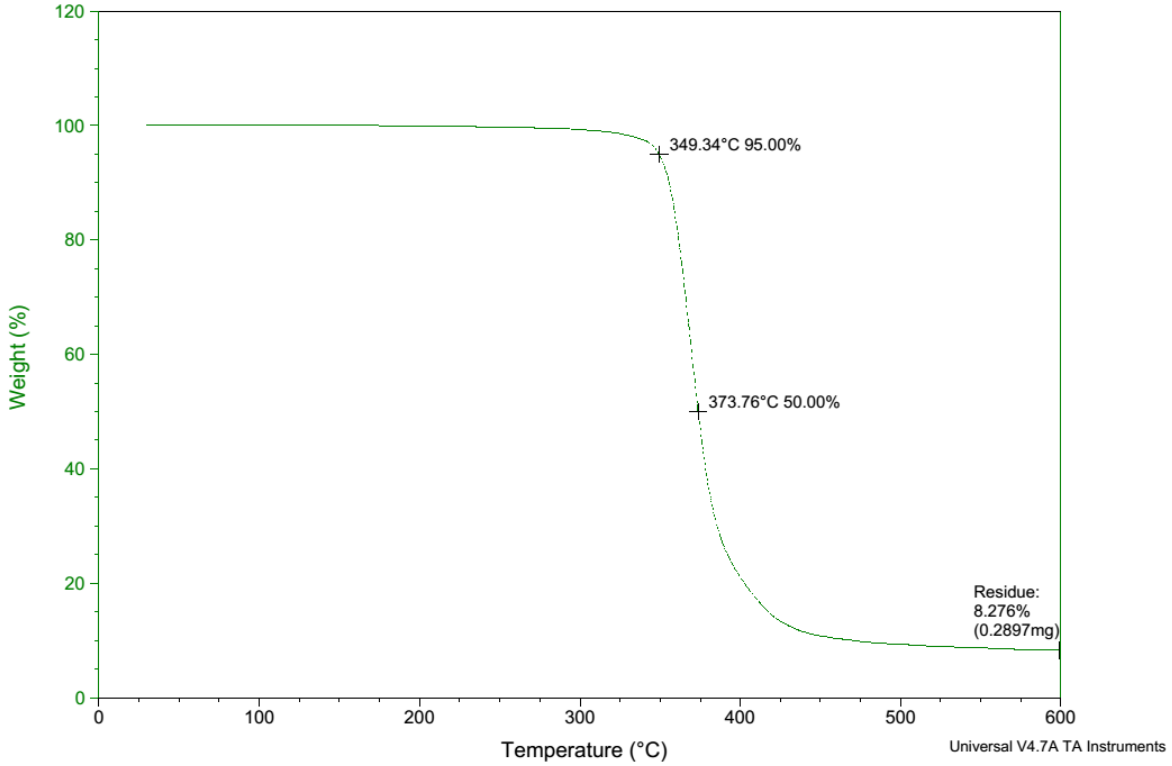


Figure S20. TGA Thermogram of **D-BB** (Table S1, entry 5).

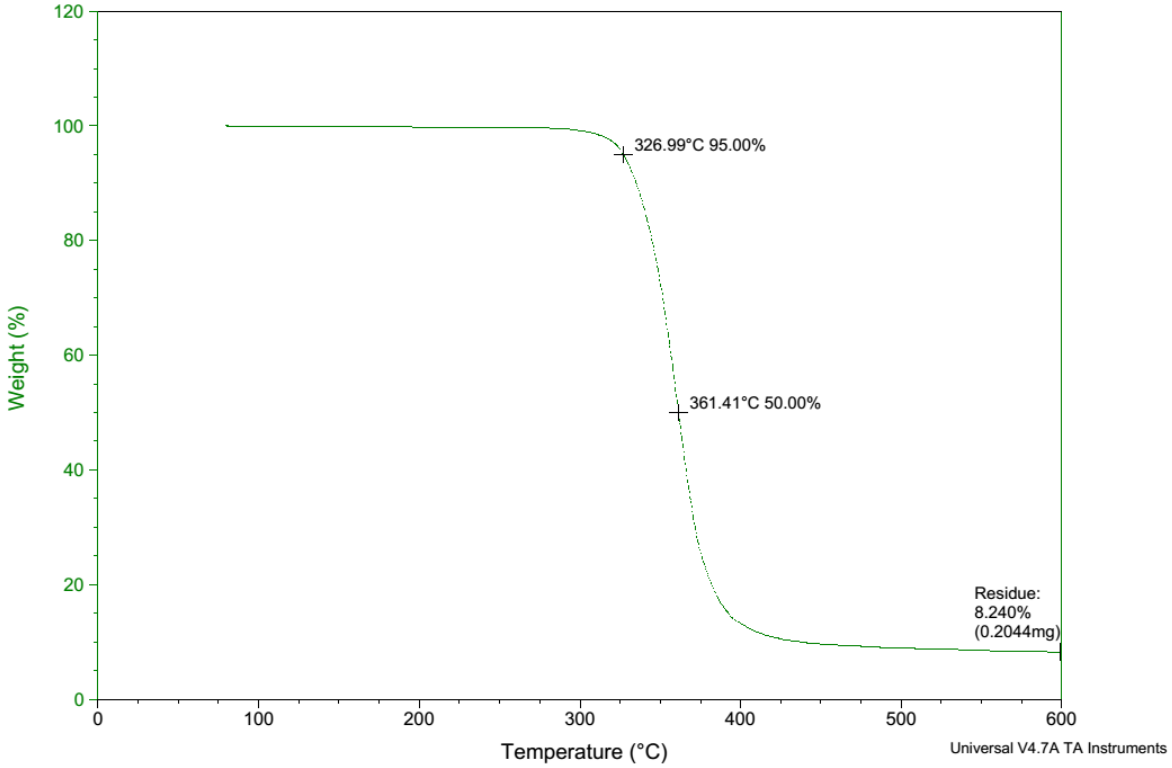


Figure S21. TGA Thermogram of **D-VV**(Table S1, entry 6).

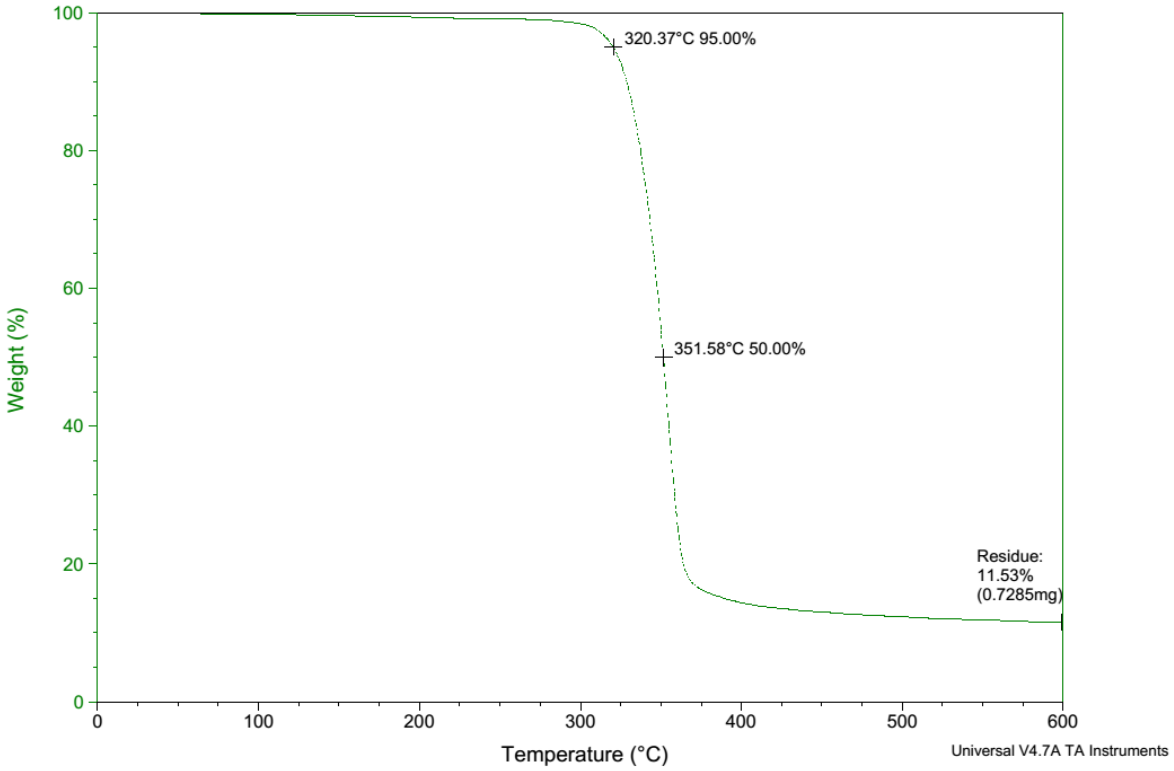


Figure S22. TGA Thermogram of **D-SS** (Table S1, entry 7).

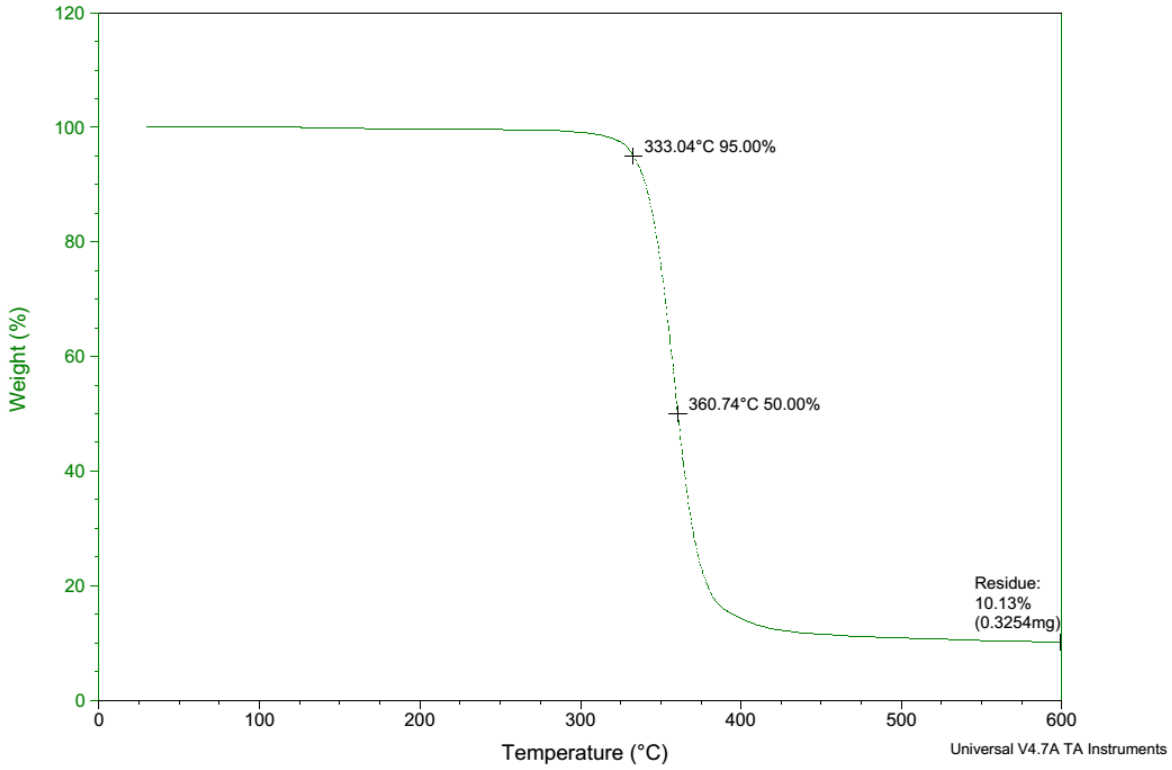


Figure S23. TGA Thermogram of **D-EE** (Table S1, entry 8).

^{1}H NMR Spectra

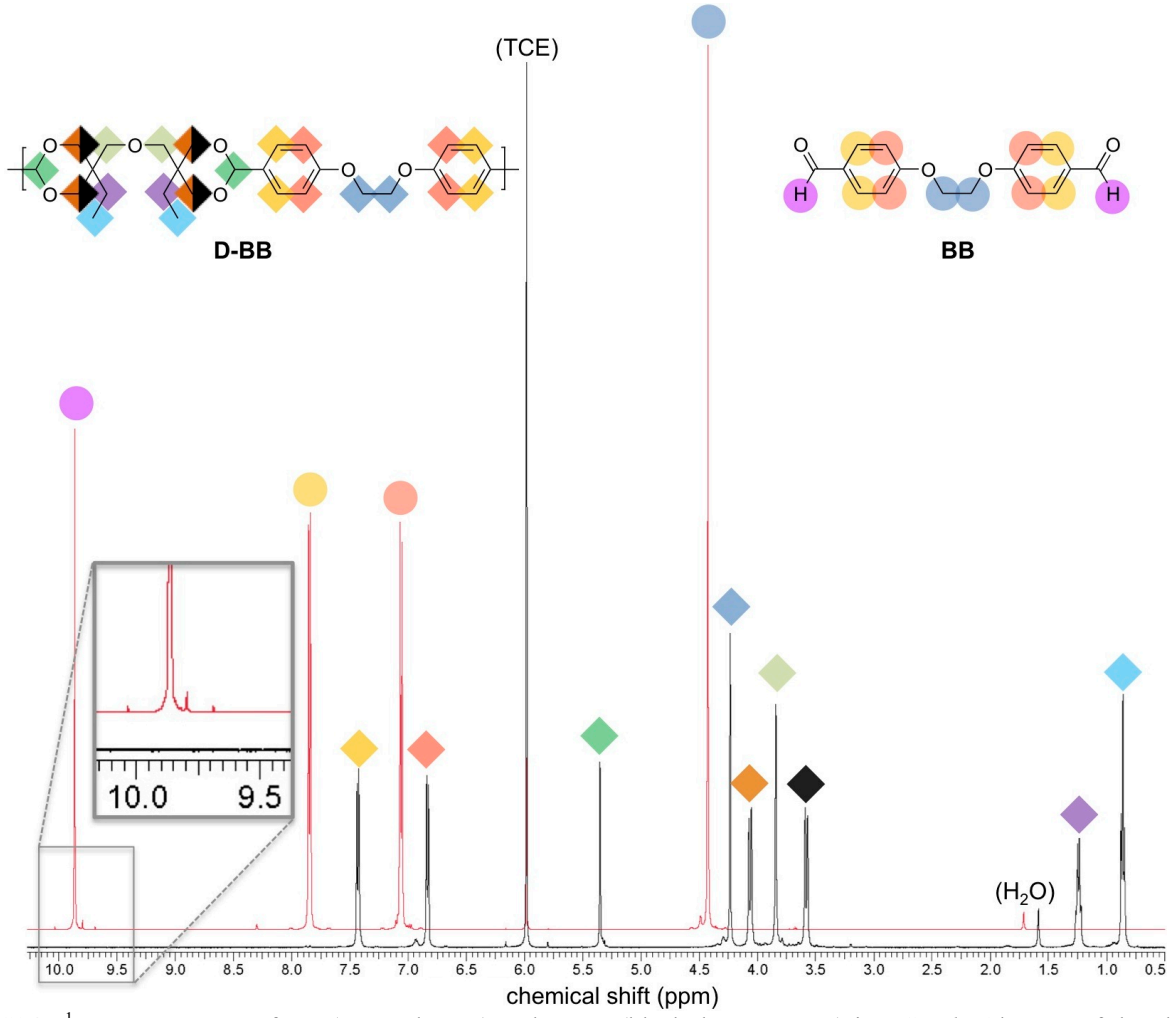


Figure S24. ^{1}H NMR spectra of **BB** (top, red trace) and **D-BB** (black, bottom trace) in TCE-d_2. Absence of the aldehydic proton (ca. 10 ppm) in the **D-BB** trace suggests that the monomer (**BB**) has been completely consumed and has been converted to high molecular weight polymer.

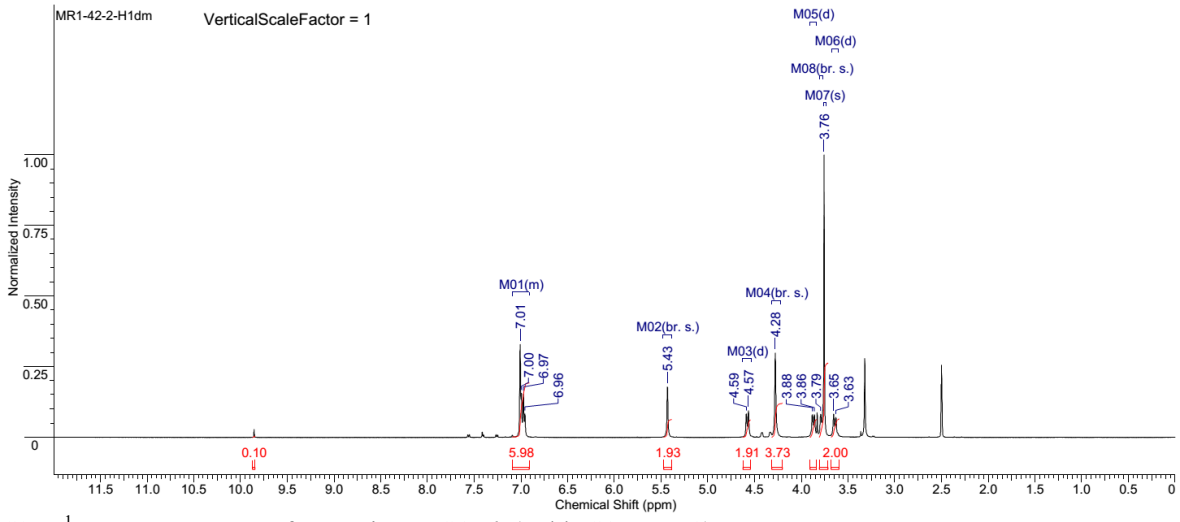


Figure S25. ^{1}H NMR spectrum of **P-VV** in DMSO-d_6 (Table S1, entry 2).

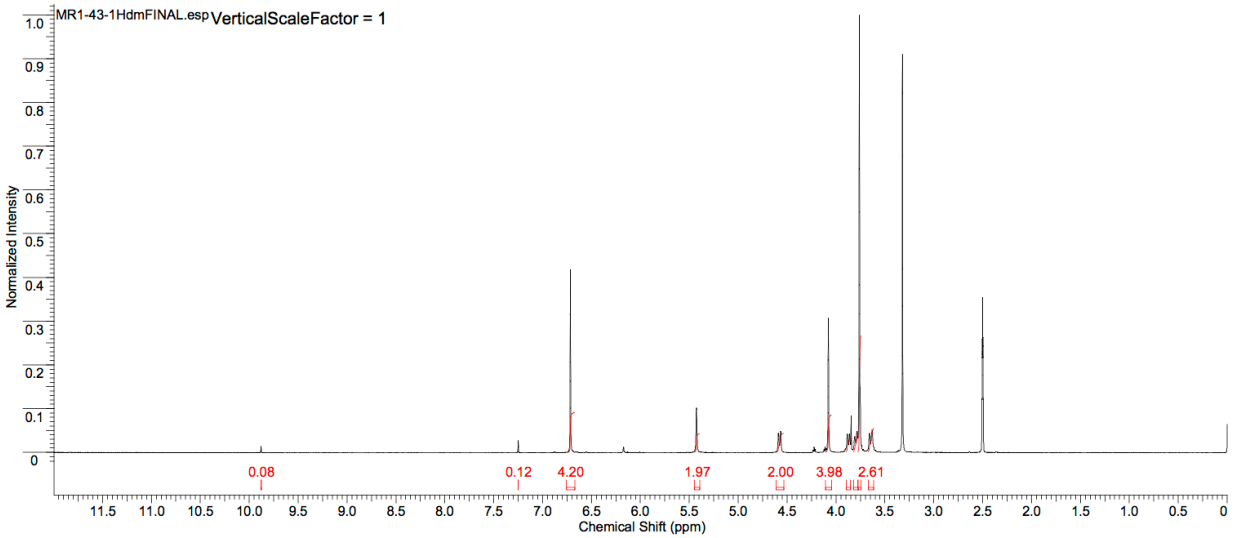


Figure S26. ^{1}H NMR spectrum of **P-SS** in DMSO-d_6 (Table S1, entry 3).

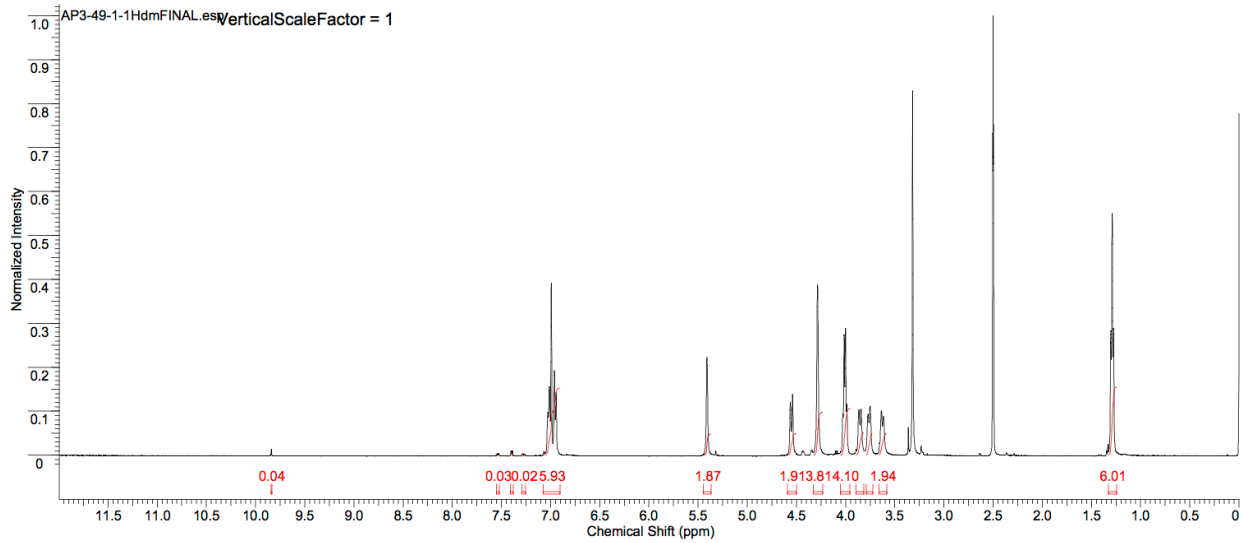


Figure S27. ^{1}H NMR spectrum of **P-EE** in DMSO-d_6 (Table S1, entry 4).

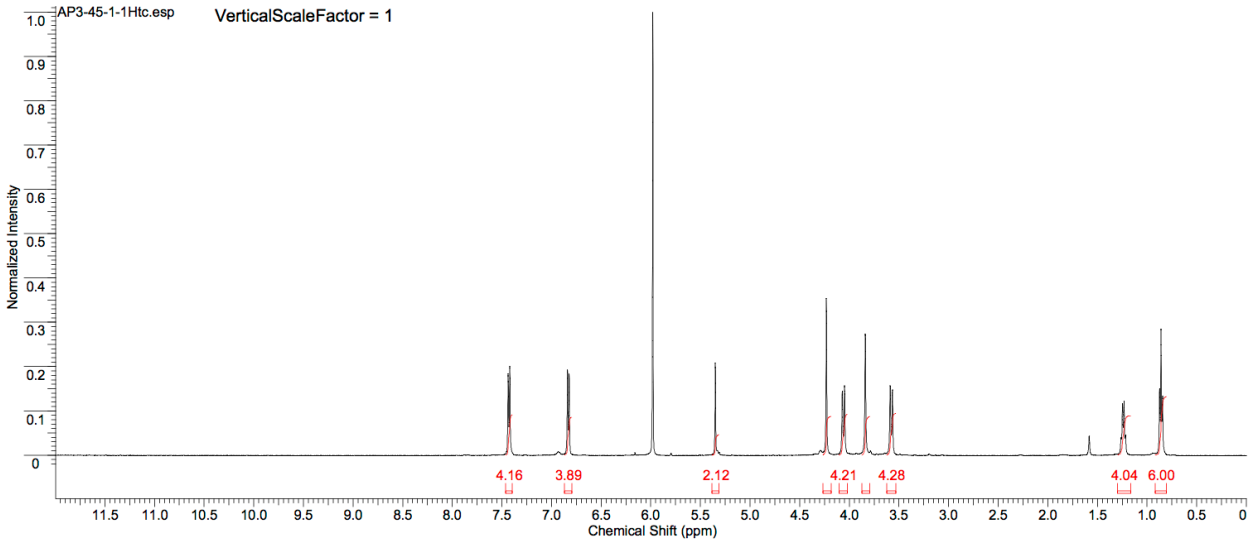


Figure S28. ^{1}H NMR spectrum of **D-BB** in TCE-d_2 (Table S1, entry 5).

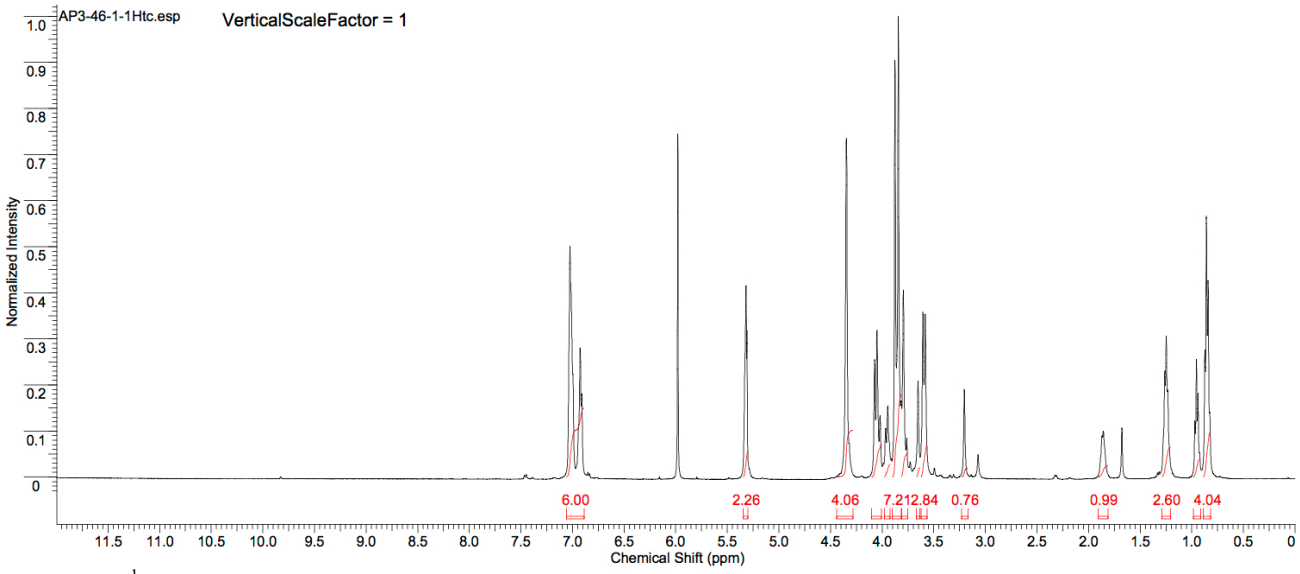


Figure S29. ^{1}H NMR spectrum of **D-VV** in TCE-d_2 (Table S1, entry 6).

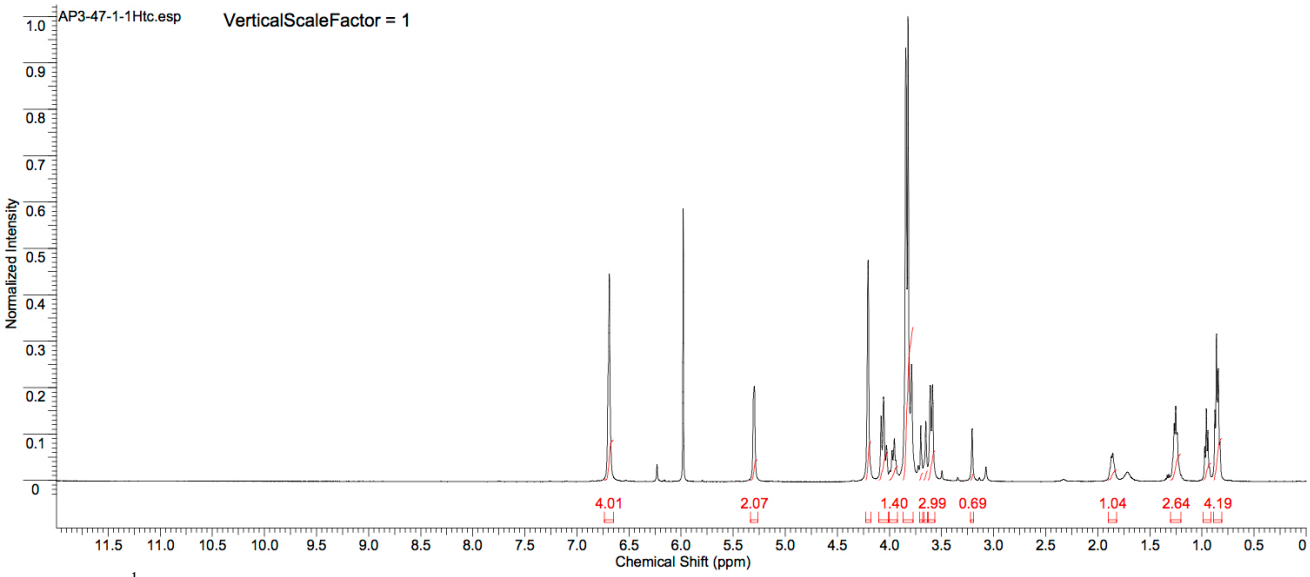


Figure S30. ^{1}H NMR spectrum of **D-SS** in TCE-d_2 (Table S1, entry 7).

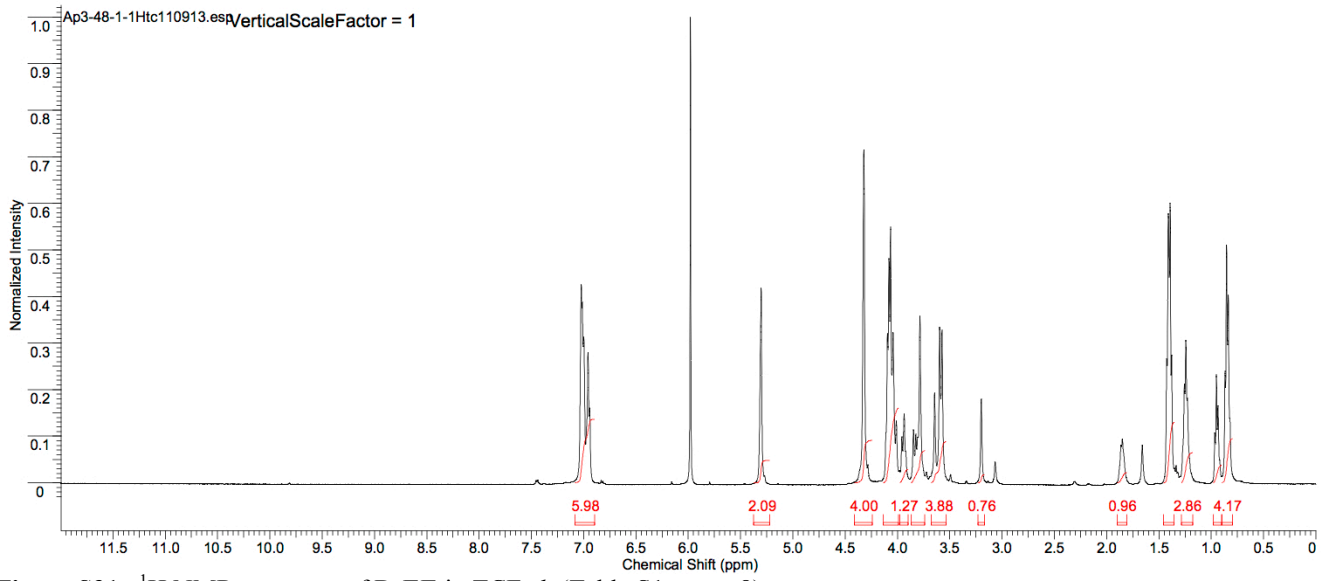


Figure S31. ^{1}H NMR spectrum of **D-EE** in TCE-d_2 (Table S1, entry 8).

^{13}C NMR Spectra

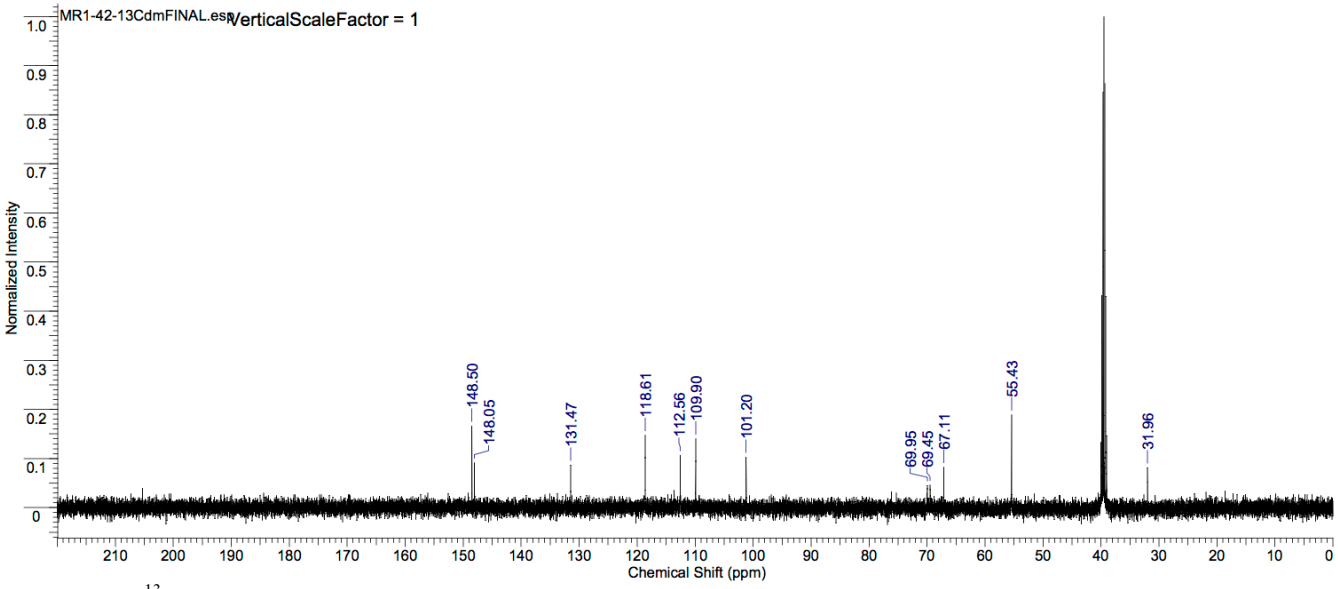


Figure S32. ^{13}C NMR spectrum of **P-VV** in DMSO-d_6 (Table S1, entry 2).

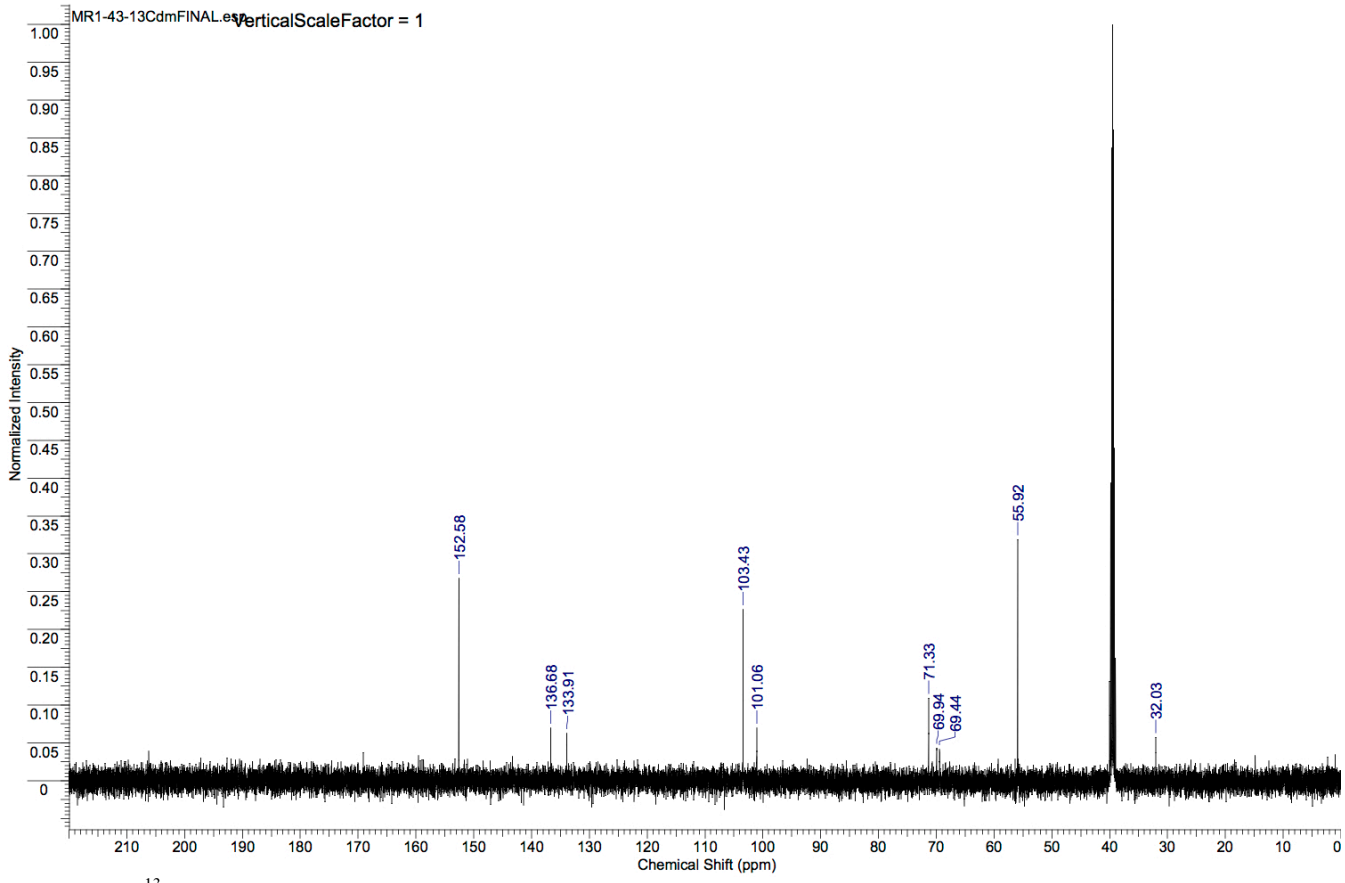


Figure S33. ^{13}C NMR spectrum of **P-SS** in DMSO-d_6 (Table S1, entry 3).

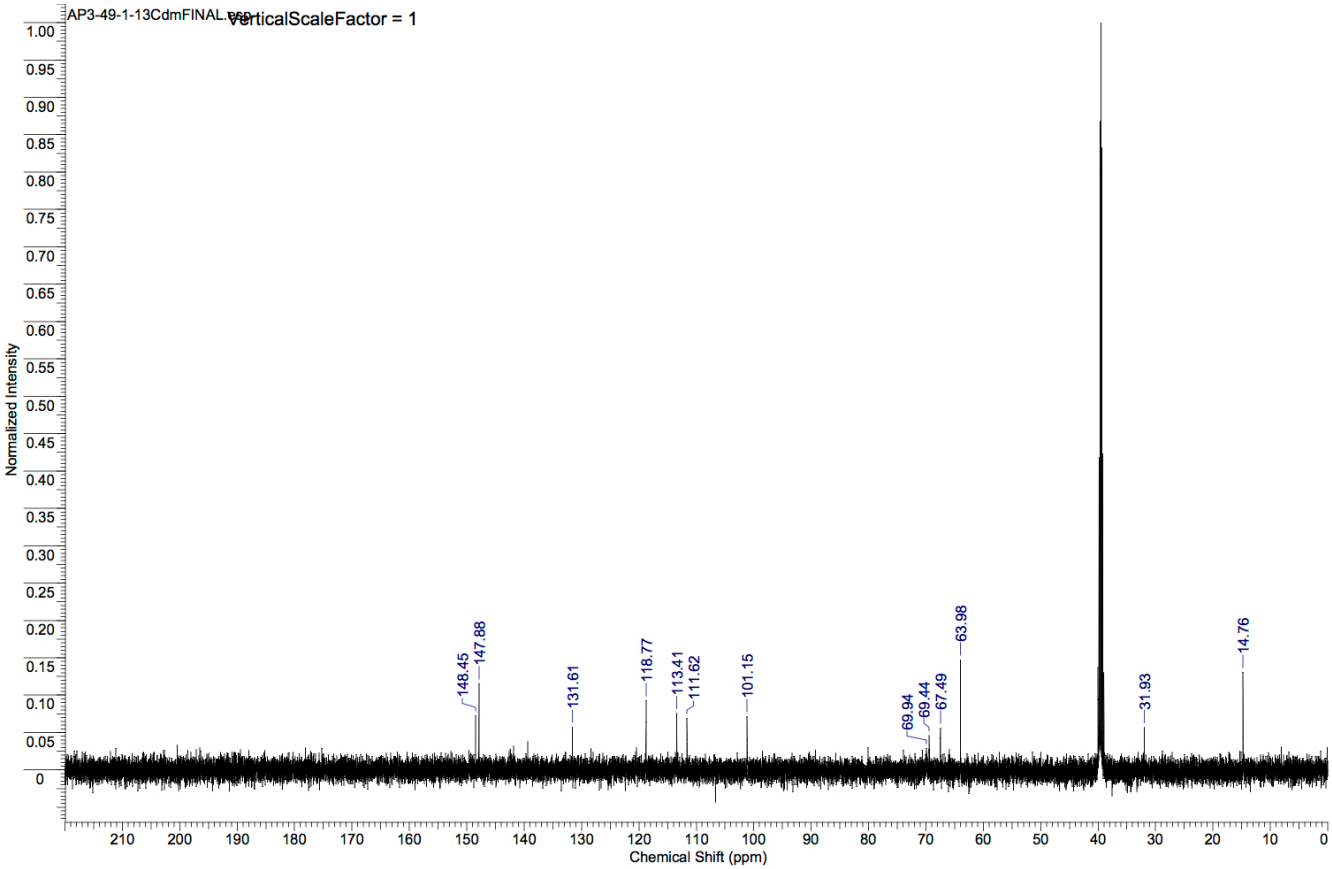


Figure S34. ^{13}C NMR spectrum of **P-EE** in DMSO-d_6 (Table S1, entry 4).

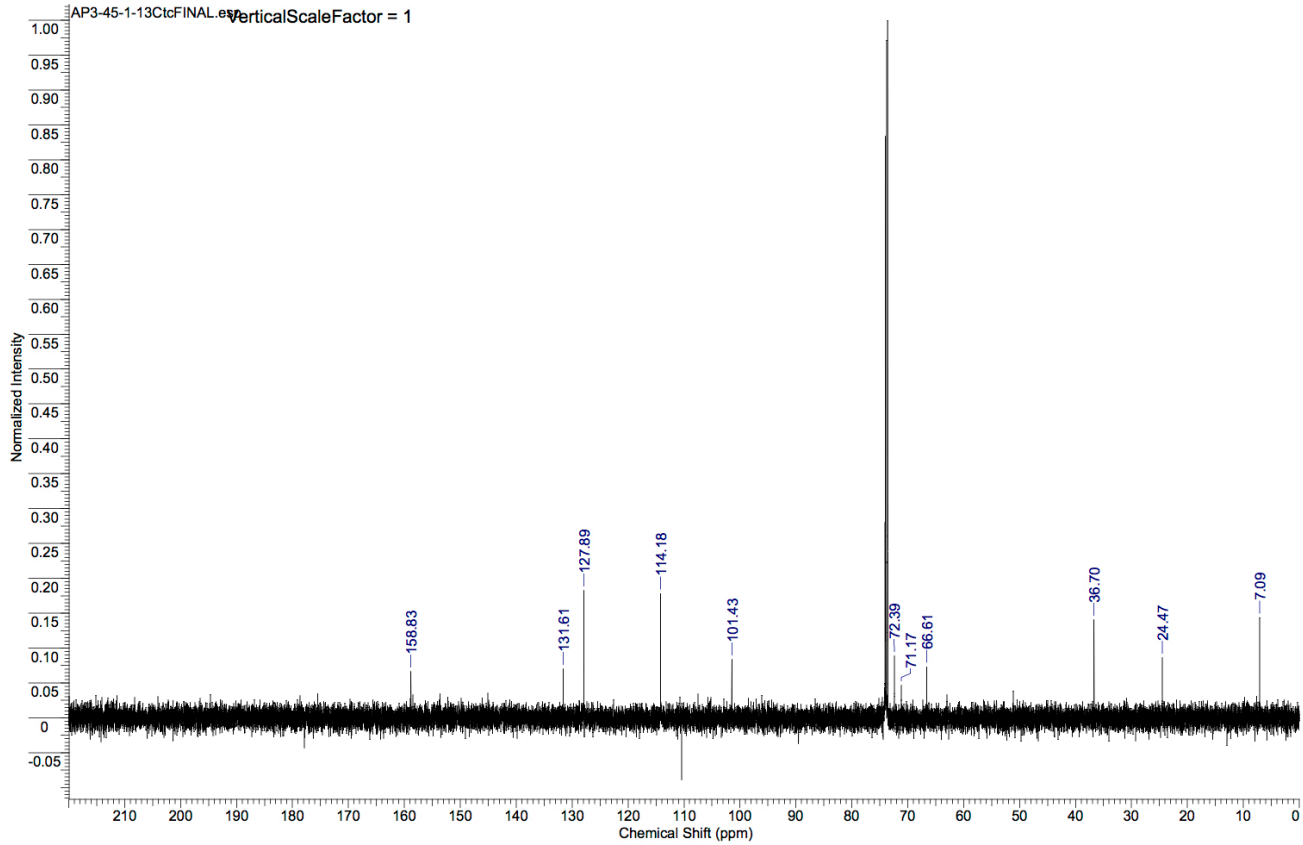


Figure S35. ^{13}C NMR spectrum of **D-BB** in TCE-d_2 (Table S1, entry 5).

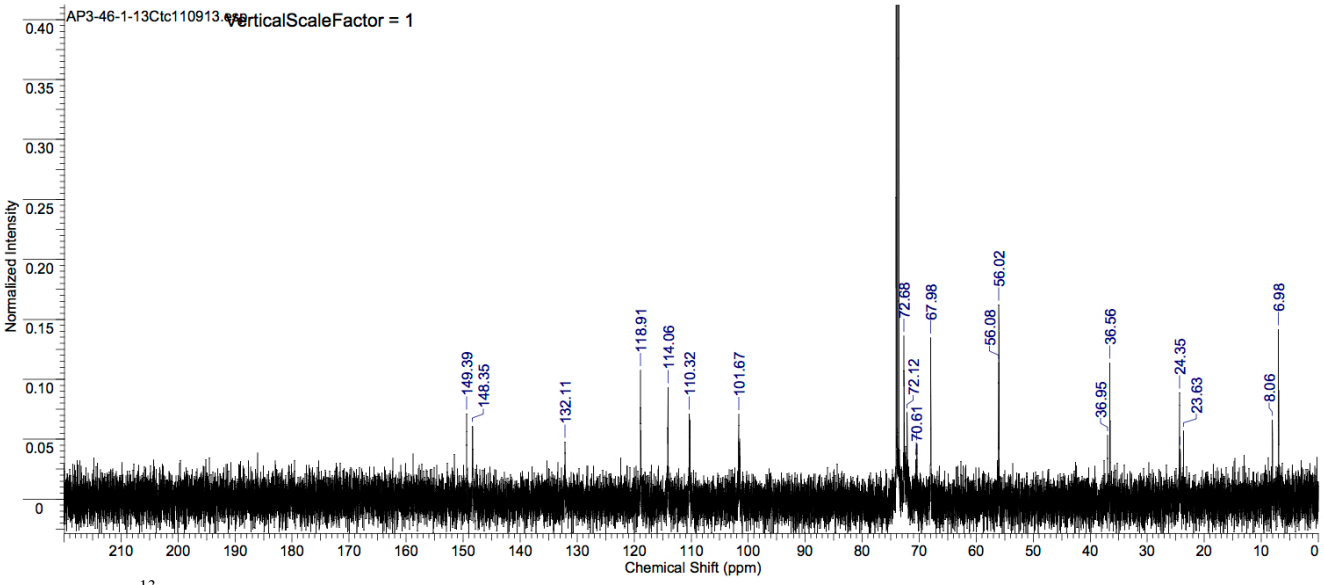


Figure S36. ^{13}C NMR spectrum of **D-VV** in TCE-d_2 (Table S1, entry 6).

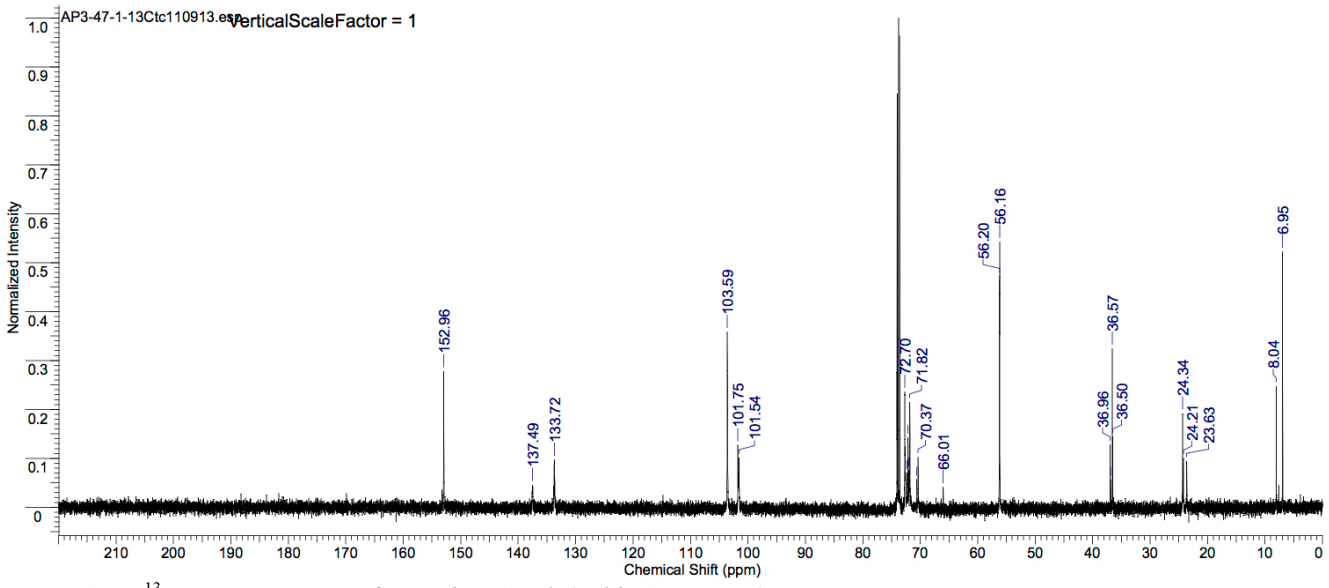


Figure S37. ^{13}C NMR spectrum of **D-SS** in TCE-d_2 (Table S1, entry 7).

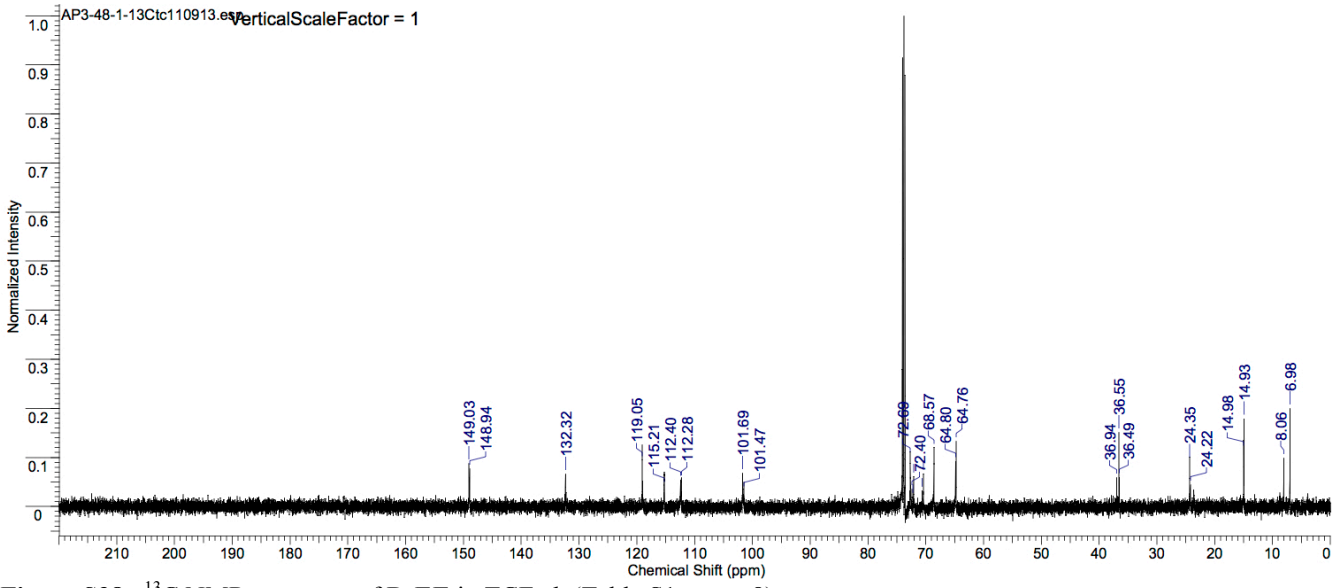


Figure S38. ^{13}C NMR spectrum of **D-EE** in TCE-d_2 (Table S1, entry 8).

Fourier Transform Infrared Spectroscopy (FTIR) Spectra

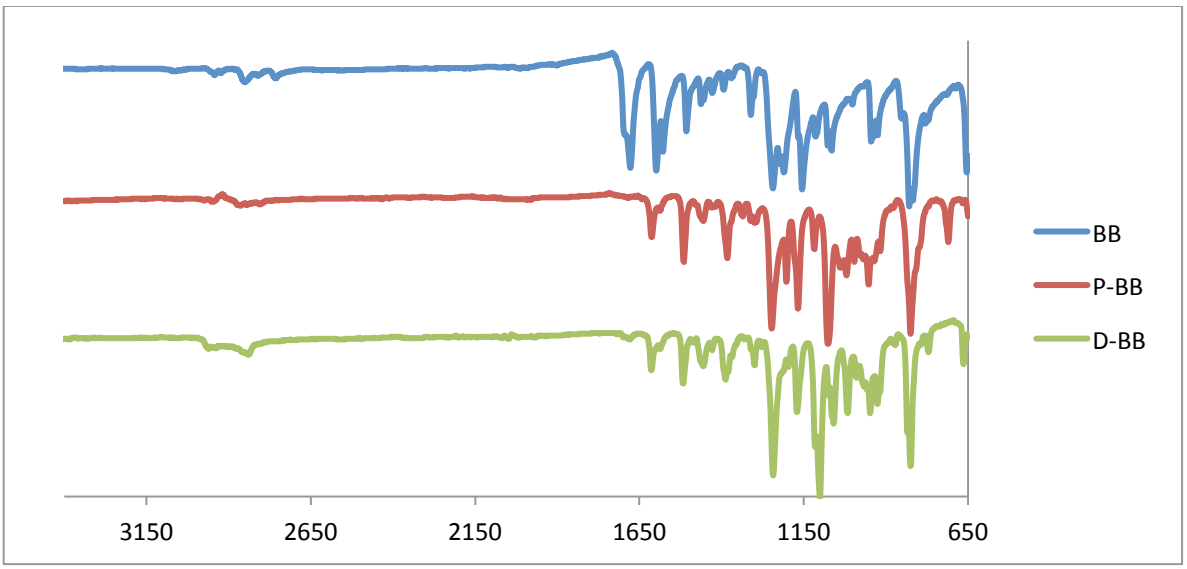


Figure S39. Comparative FTIR spectra for **BB** (monomer), **P-BB**, and **D-BB** .

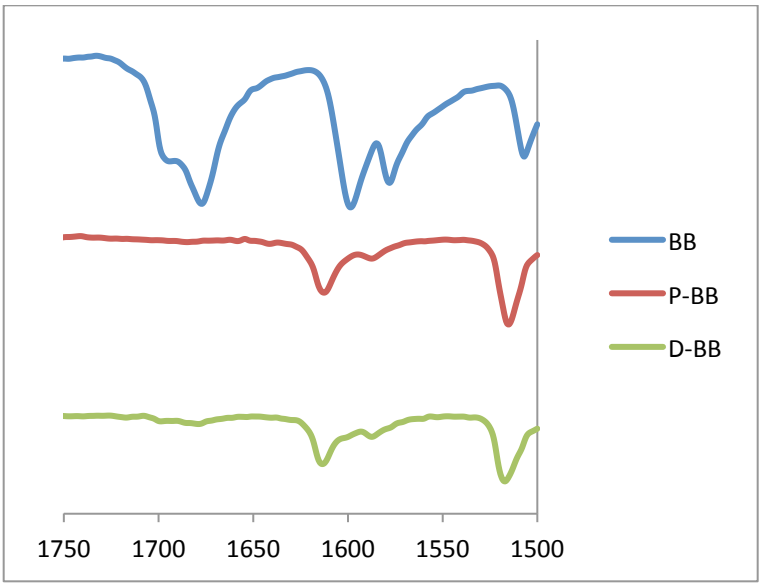


Figure S40. Comparative FTIR spectra for **BB** (monomer), **P-BB**, and **D-BB** for carbonyl area (magnified), showing no carbonyl peak in either polymer.

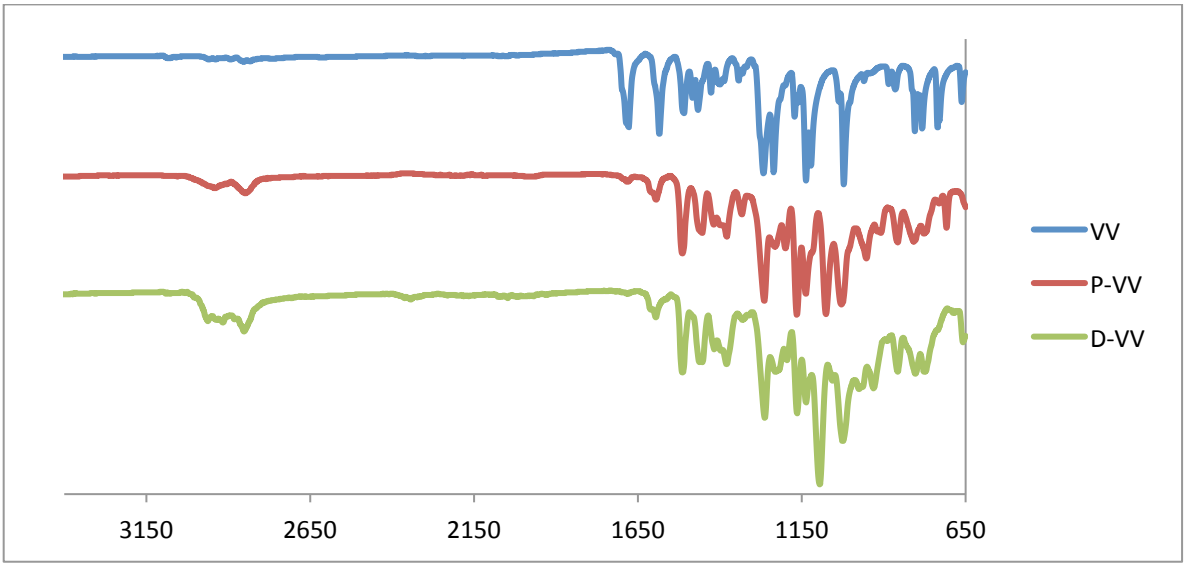


Figure S41. Comparative FTIR spectra for **VV** (monomer), **P-VV**, and **D-VV**.

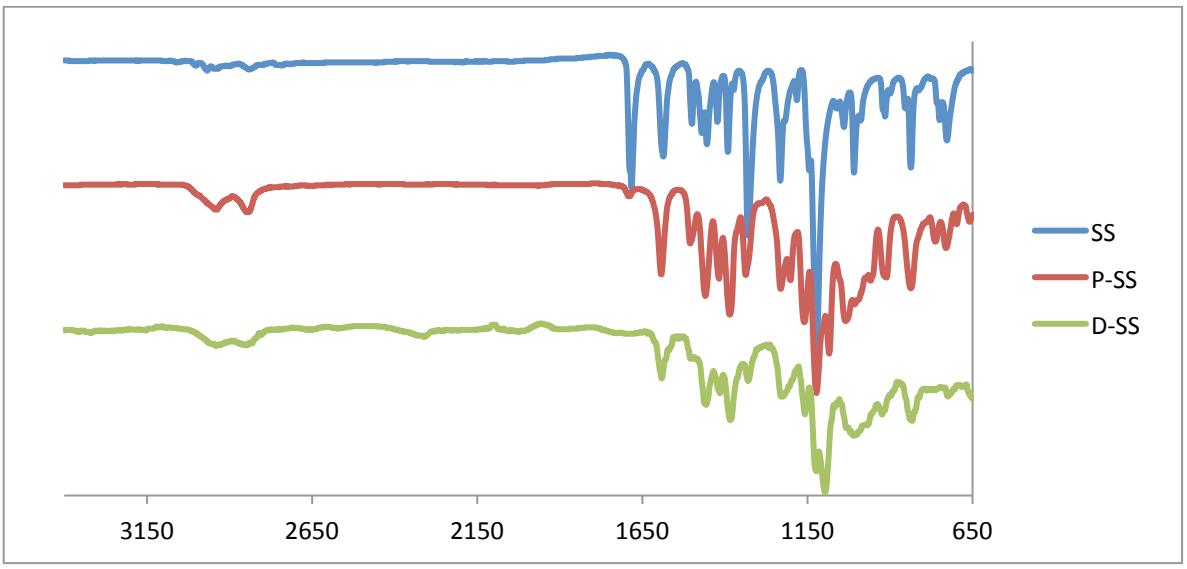


Figure S42. Comparative FTIR spectra for **SS** (monomer), **P-SS**, and **D-SS** .

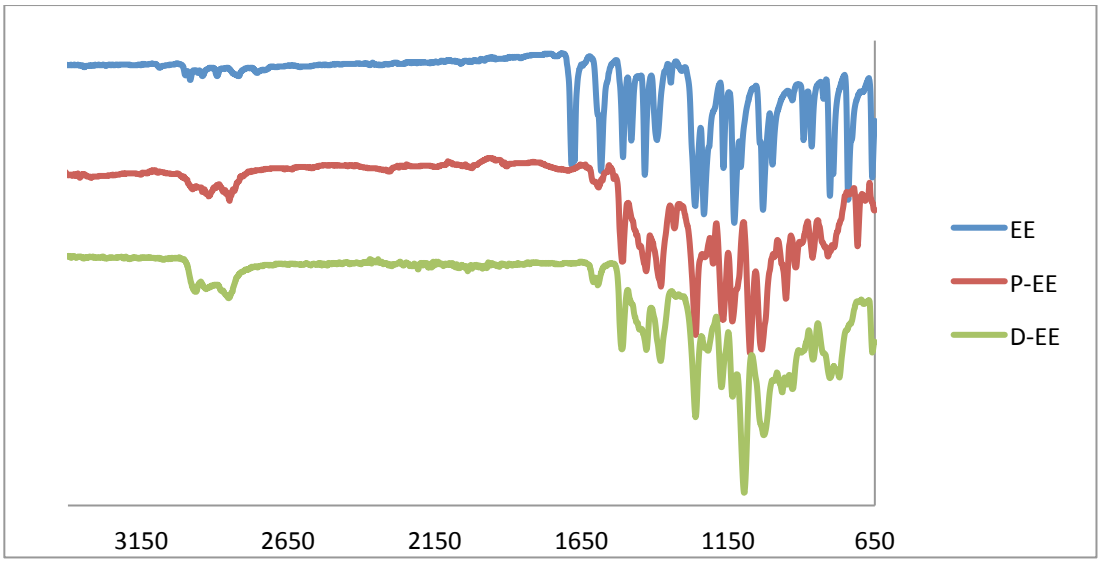


Figure S43. Comparative FTIR spectra for **EE** (monomer), **P-EE**, and **D-EE** .

Degradation Studies via Dynamic Light Scattering (DLS)

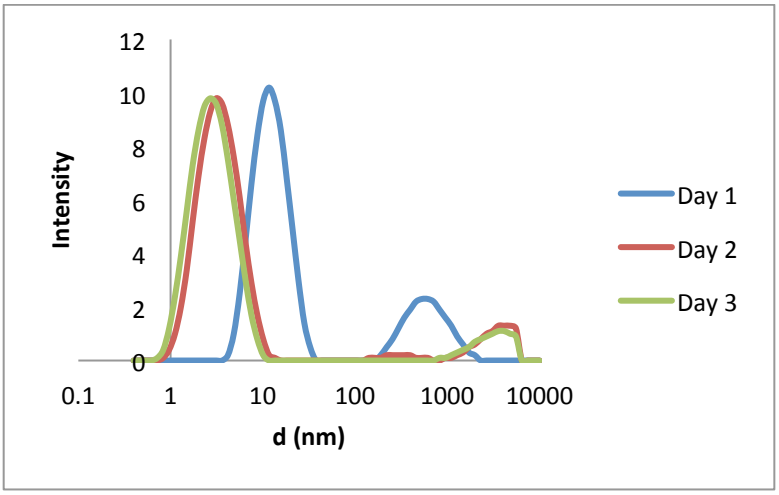


Figure S44. Degradation studies of **P-VV** / DMSO solution with 0.5% aqueous concentrated HCl.

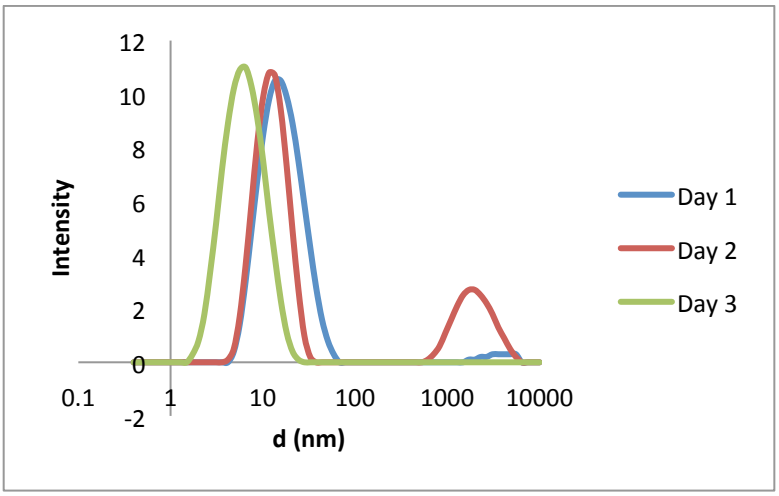


Figure S45. Degradation studies of **P-VV** / DMSO solution with 0.5% 2M aqueous HCl.

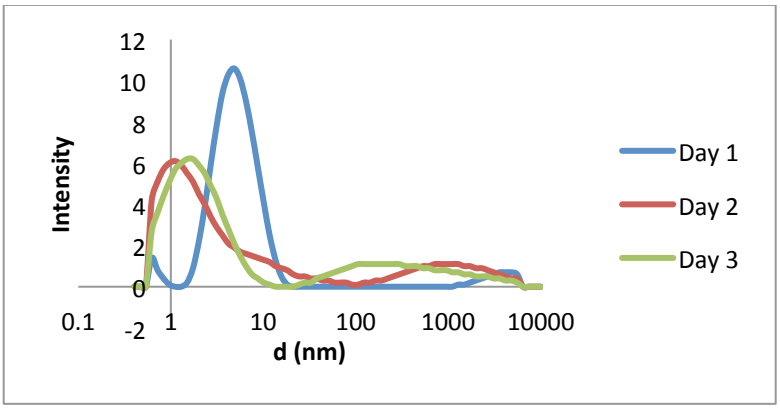


Figure S46. Degradation studies of **D-VV** / DMSO solution with 0.5% aqueous concentrated HCl.

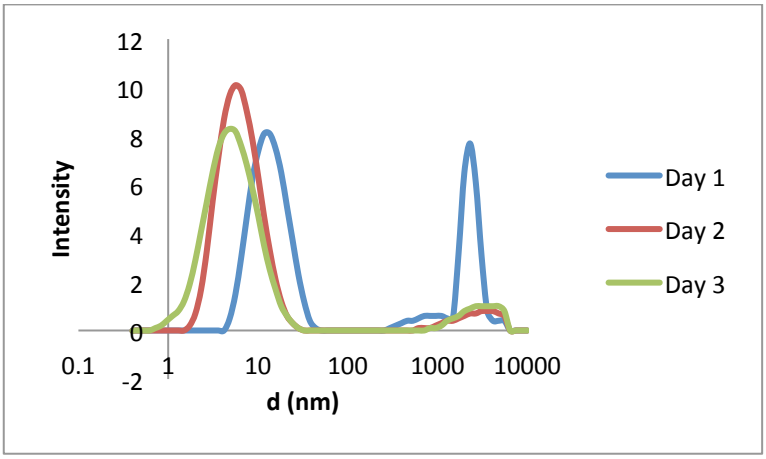


Figure S47. Degradation studies of **D-VV** / DMSO solution with 0.5% 2M aqueous HCl.