

Electronic Supplementary Information

Selective transesterification mediated by lanthanum complexes in the copolymerisation of lactide and δ - valerolactone

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1. NMR Spectra of Copolymers

Figure S1: ^1H NMR Spectrum of polymer from Table 2, entry 1

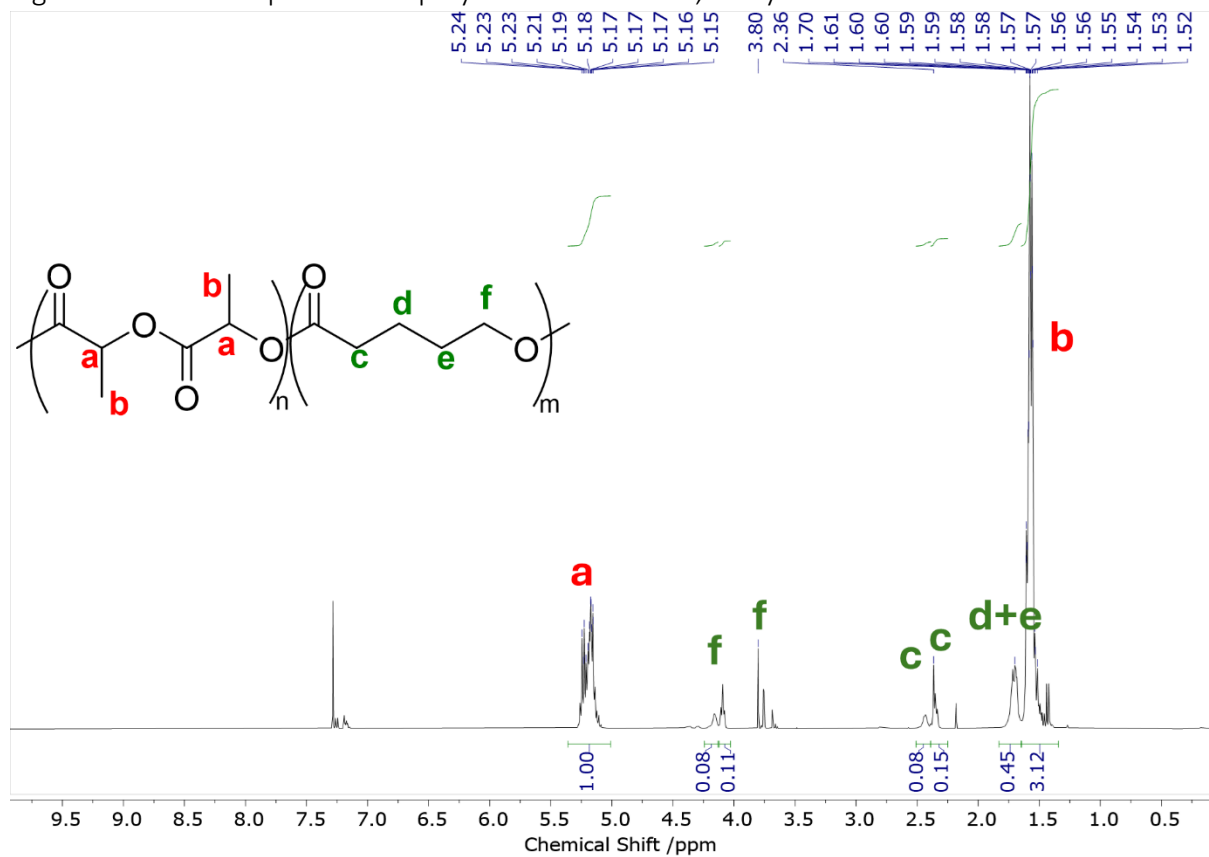


Figure S2: ^1H NMR Spectrum of polymer from Table 2, entry 2

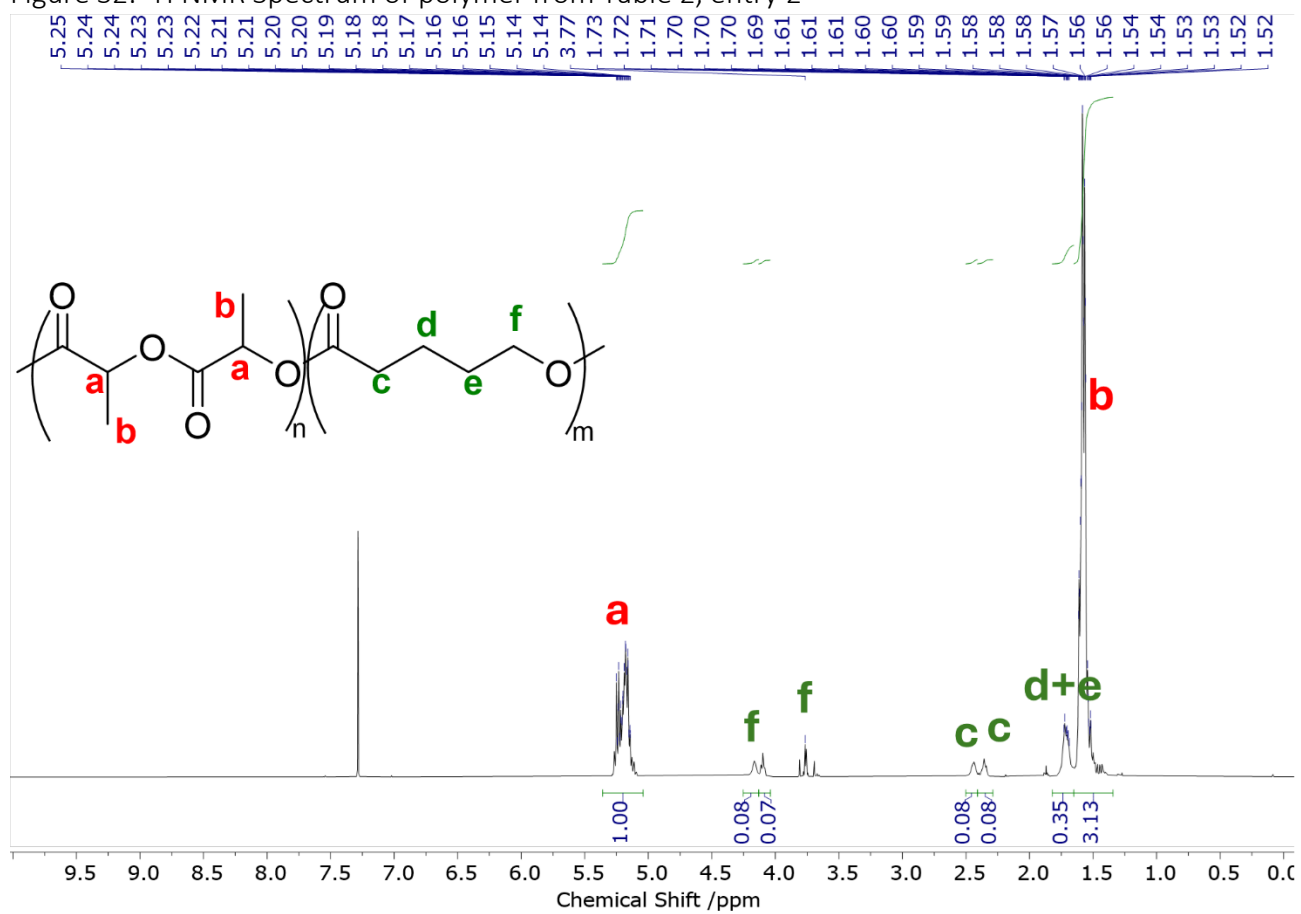


Figure S3: ^1H NMR Spectrum of polymer from Table 2, entry 3

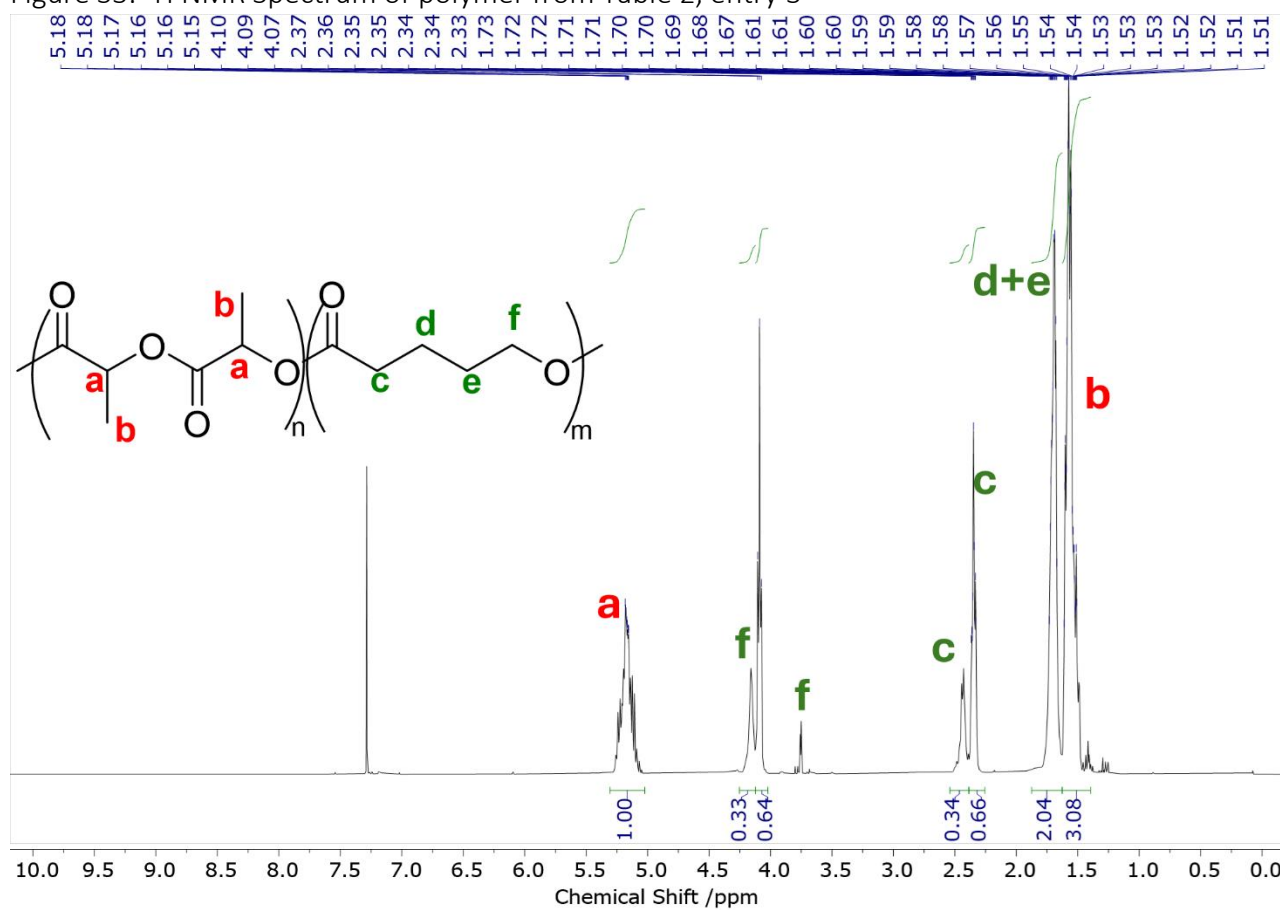


Figure S4: ^1H NMR Spectrum of polymer from Table 2, entry 4

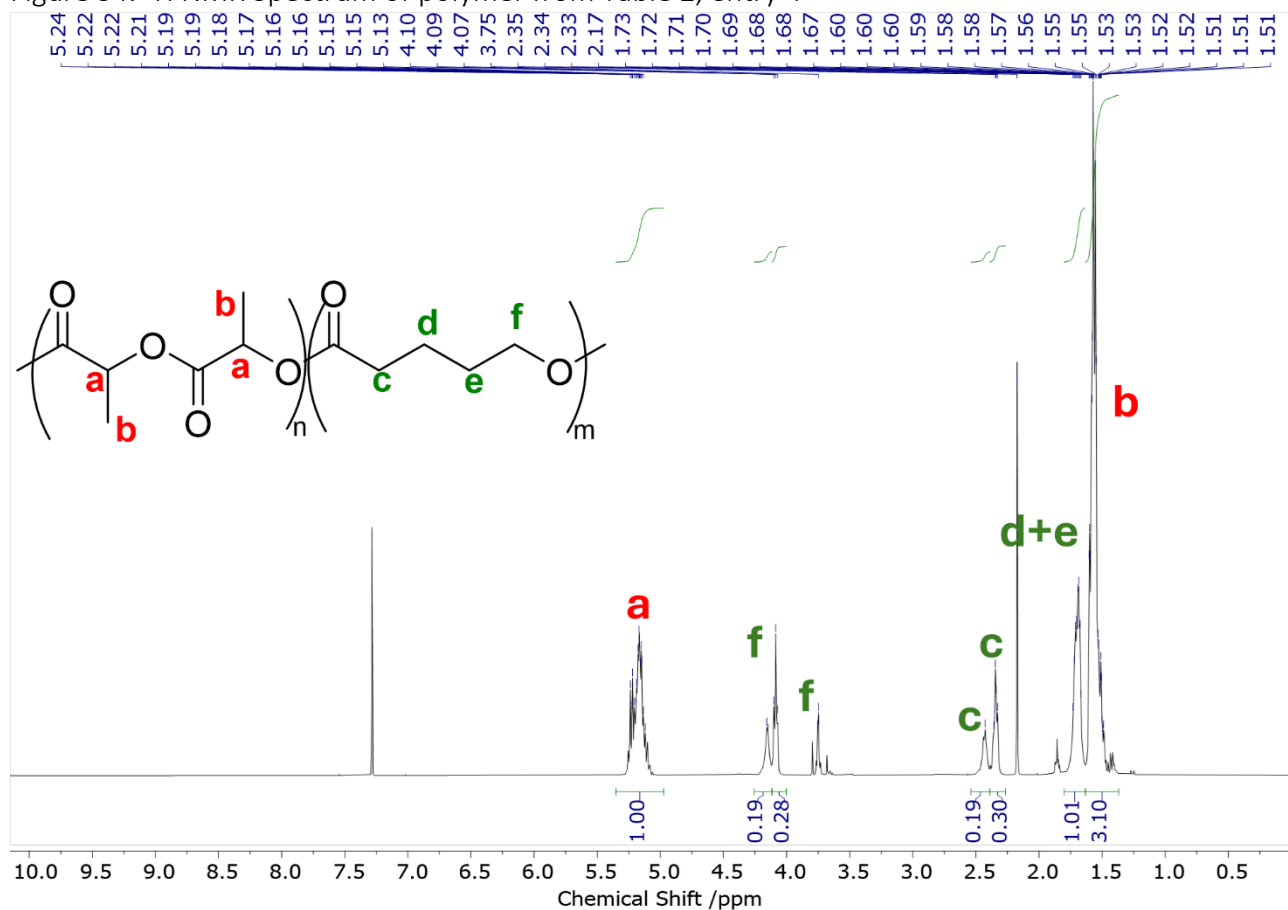


Figure S5: ^1H NMR Spectrum of polymer from Table 2, entry 5

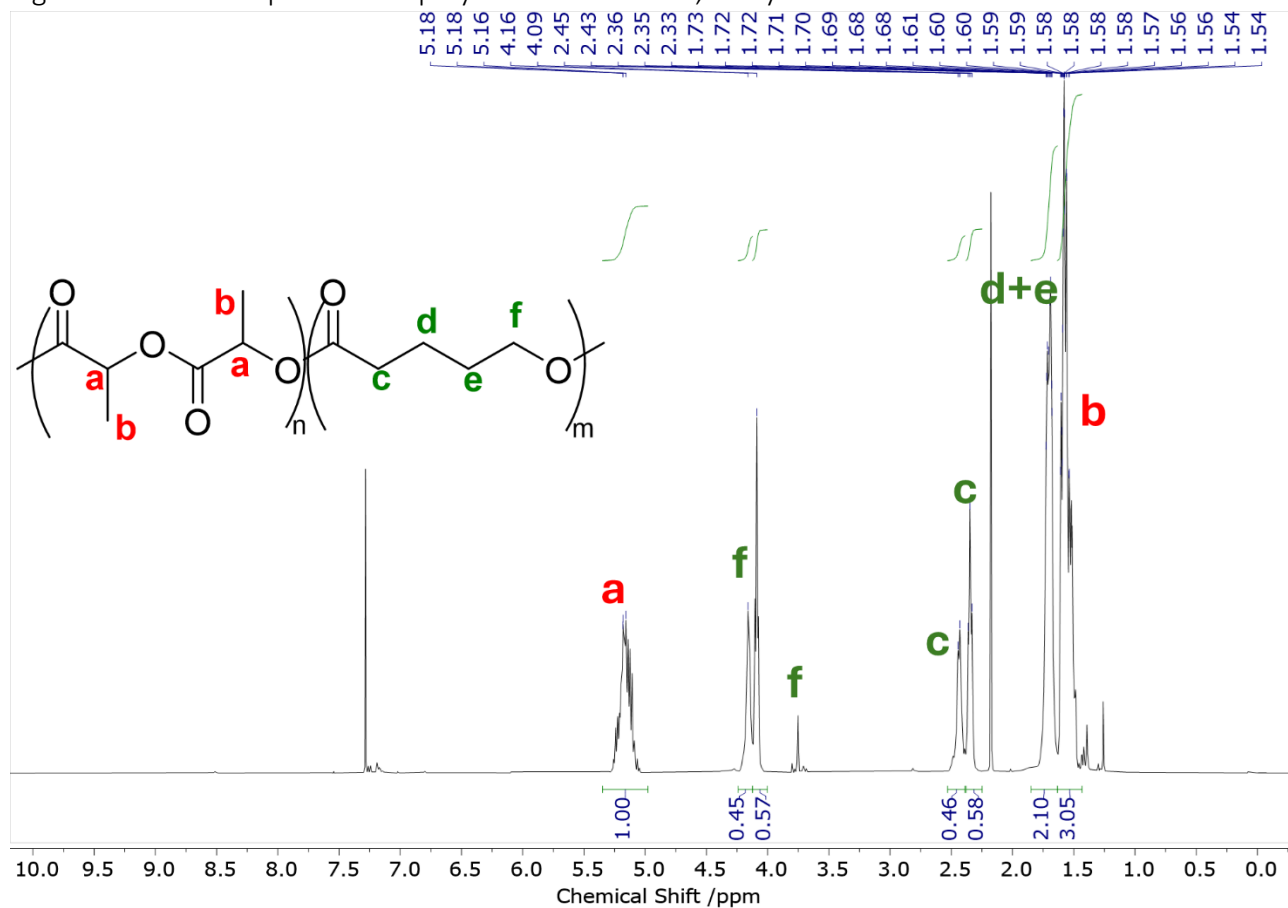


Figure S6: ^1H NMR Spectrum of polymer from Table 2, entry 6

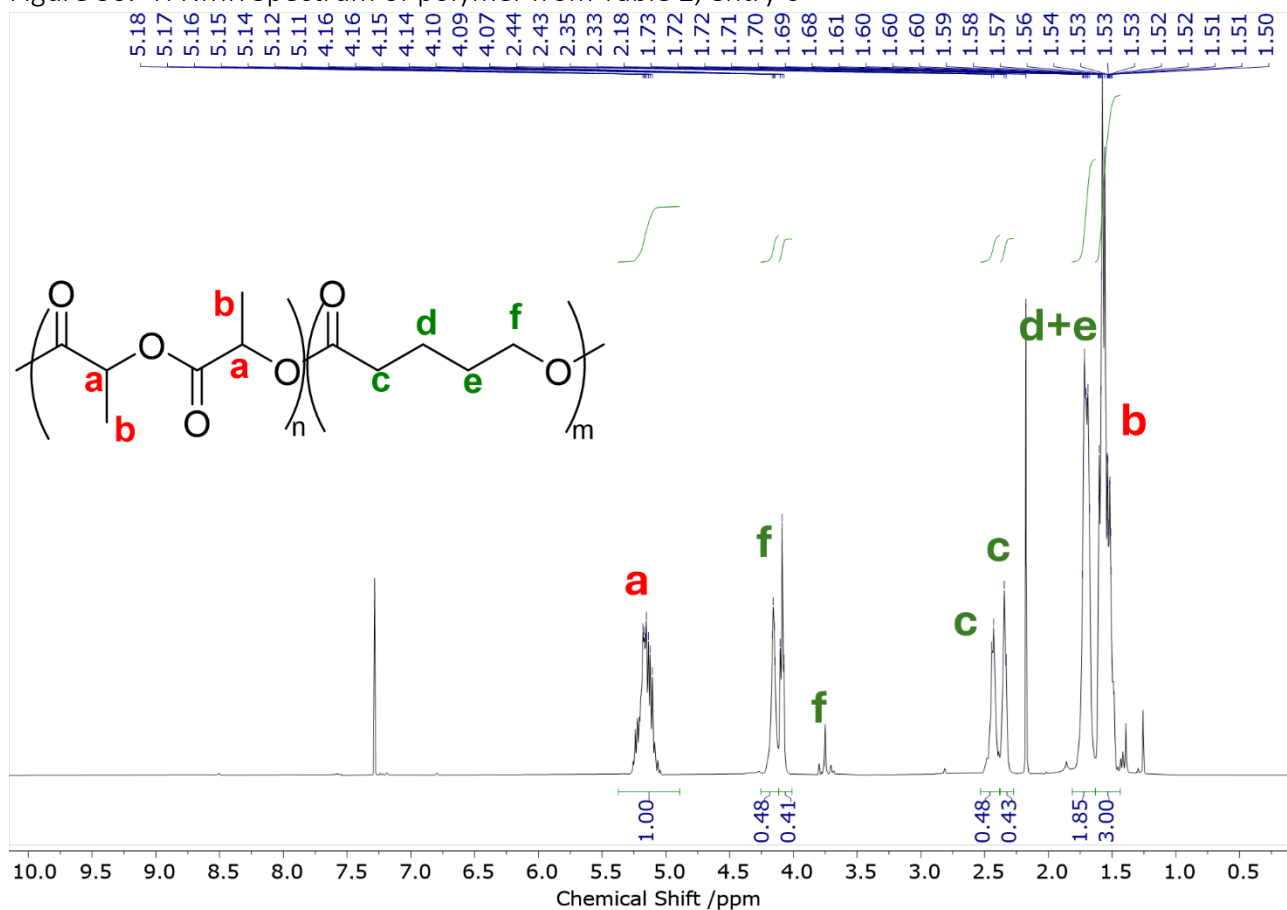


Figure S7: ^1H NMR Spectrum of polymer from Table 2, entry 7

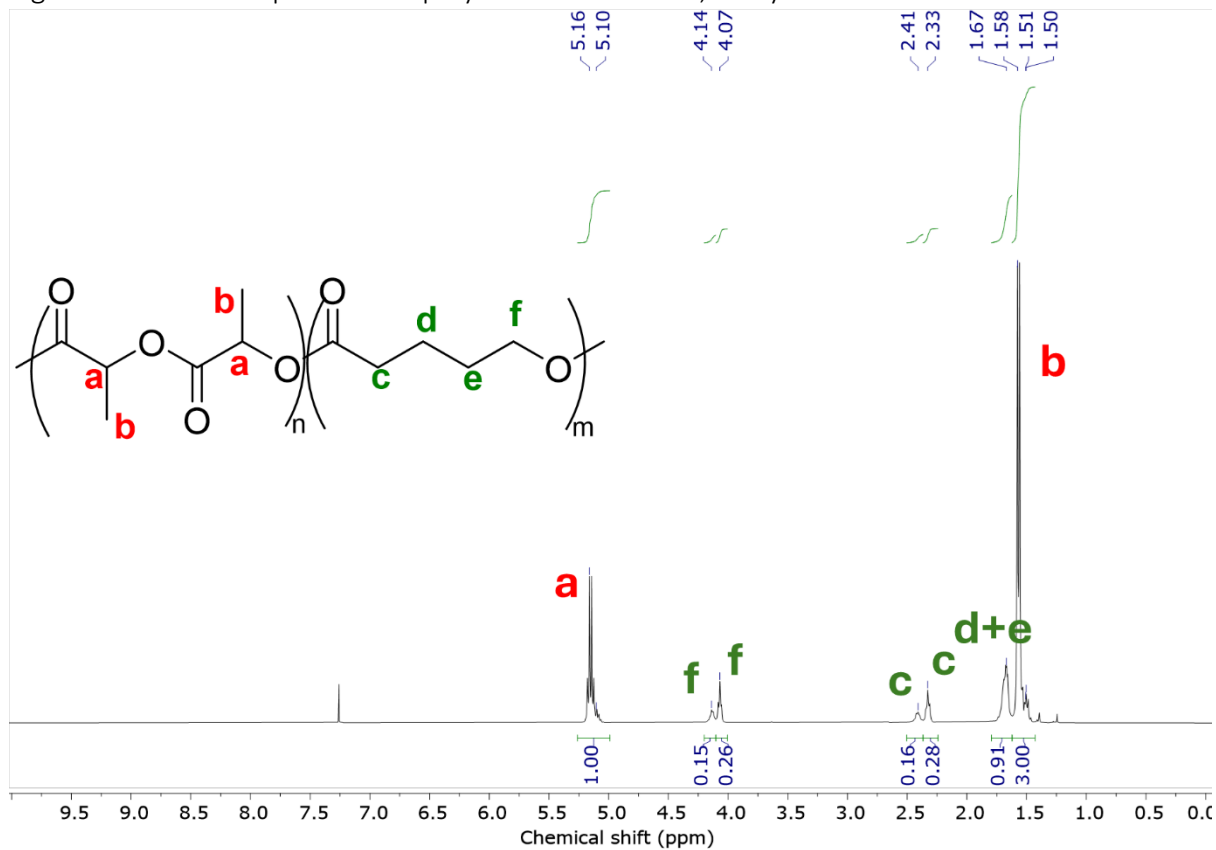


Figure S8: ^1H NMR Spectrum of polymer from Table 2, entry 8

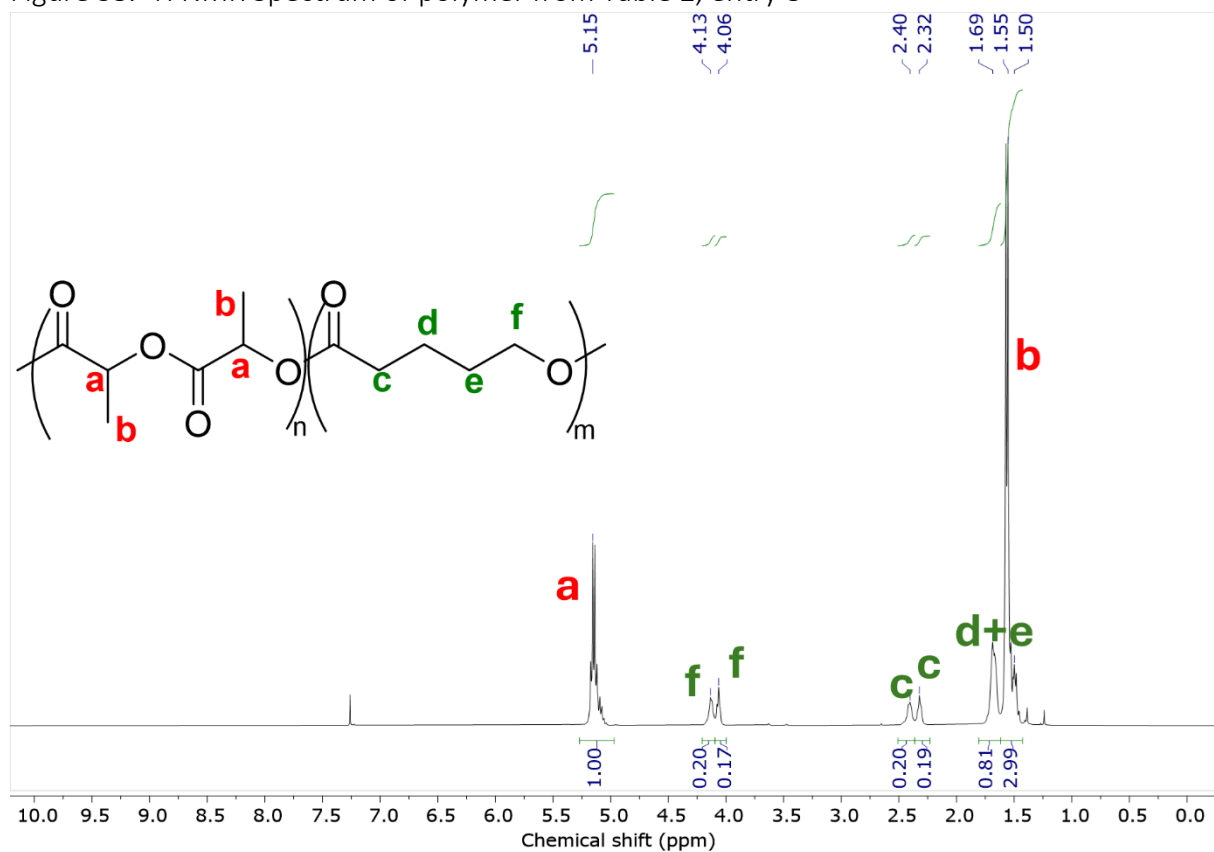


Figure S9: ^1H NMR Spectrum of polymer from Table 2, entry 9

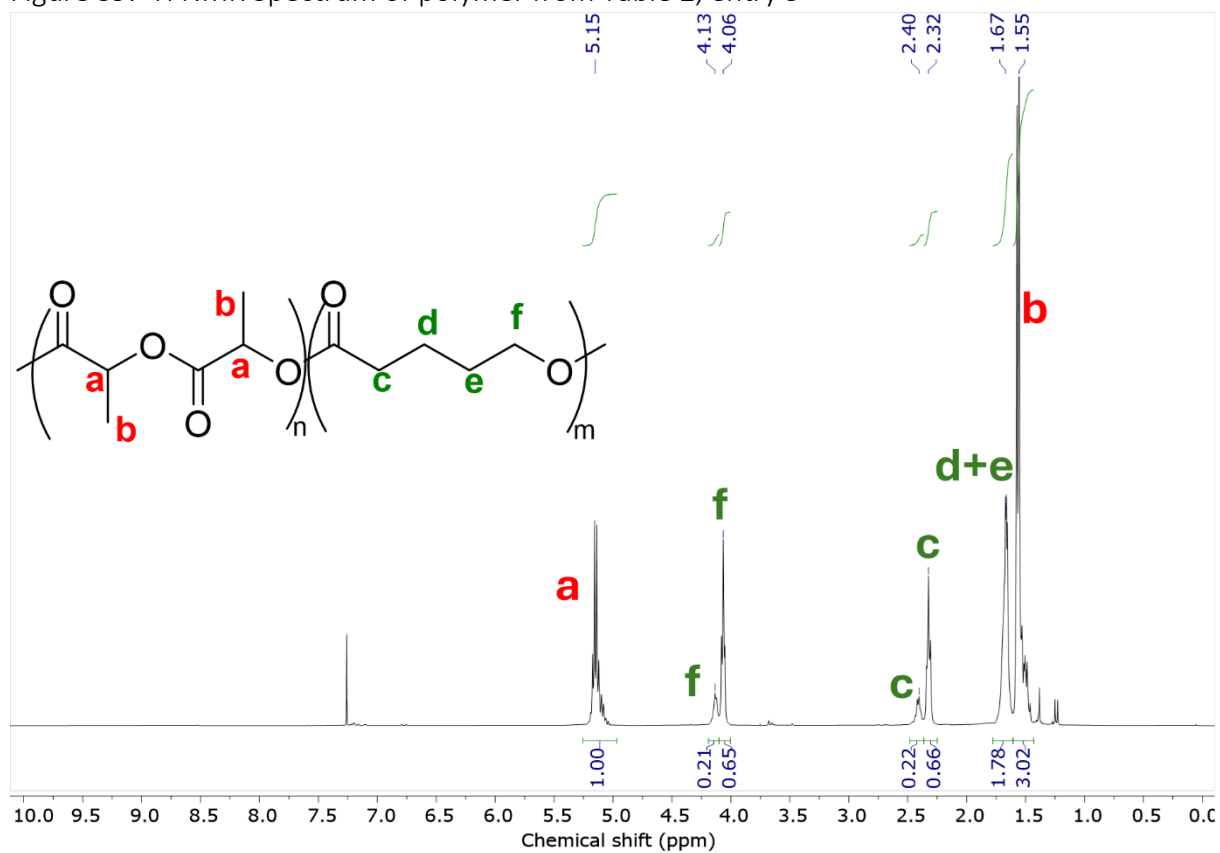


Figure S10: ^1H NMR Spectrum of polymer from Table 2, entry 10

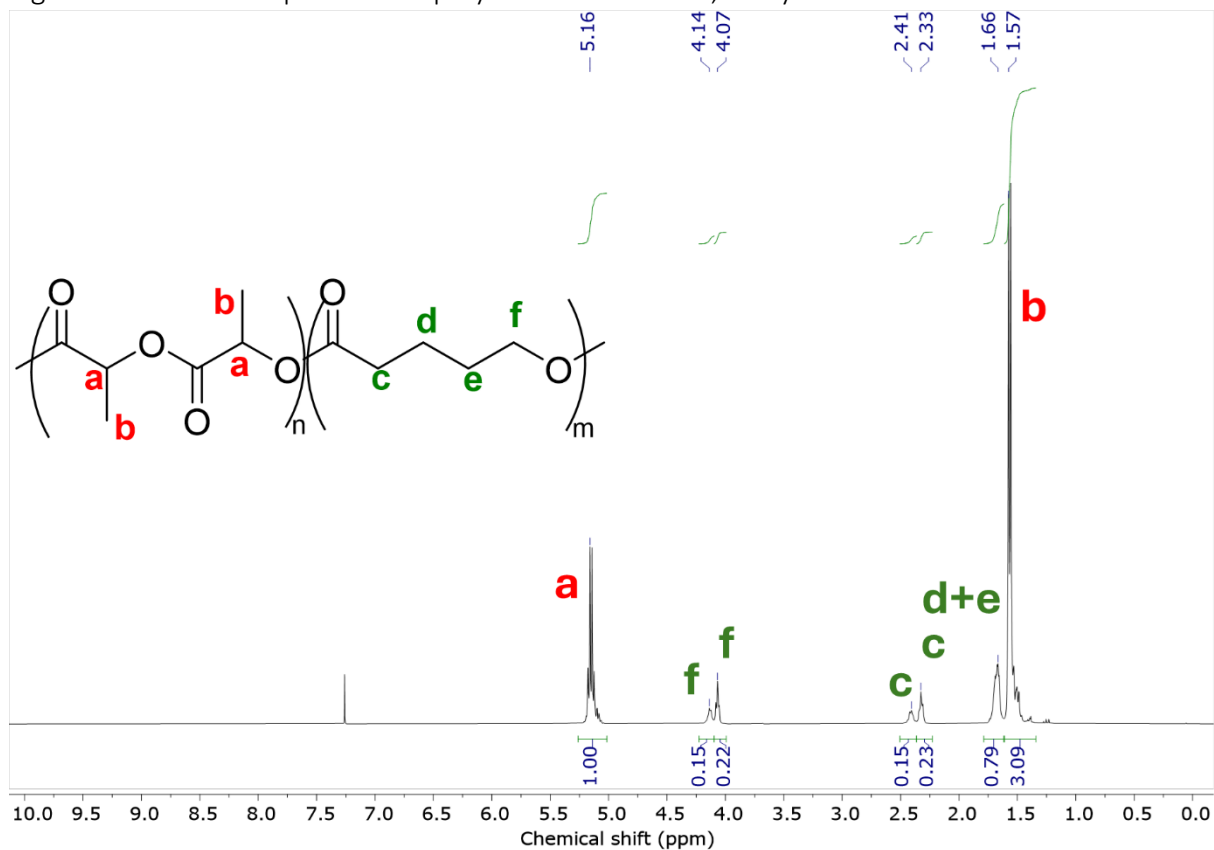


Figure S12: ^1H NMR Spectrum of polymer from Table 2, entry 11

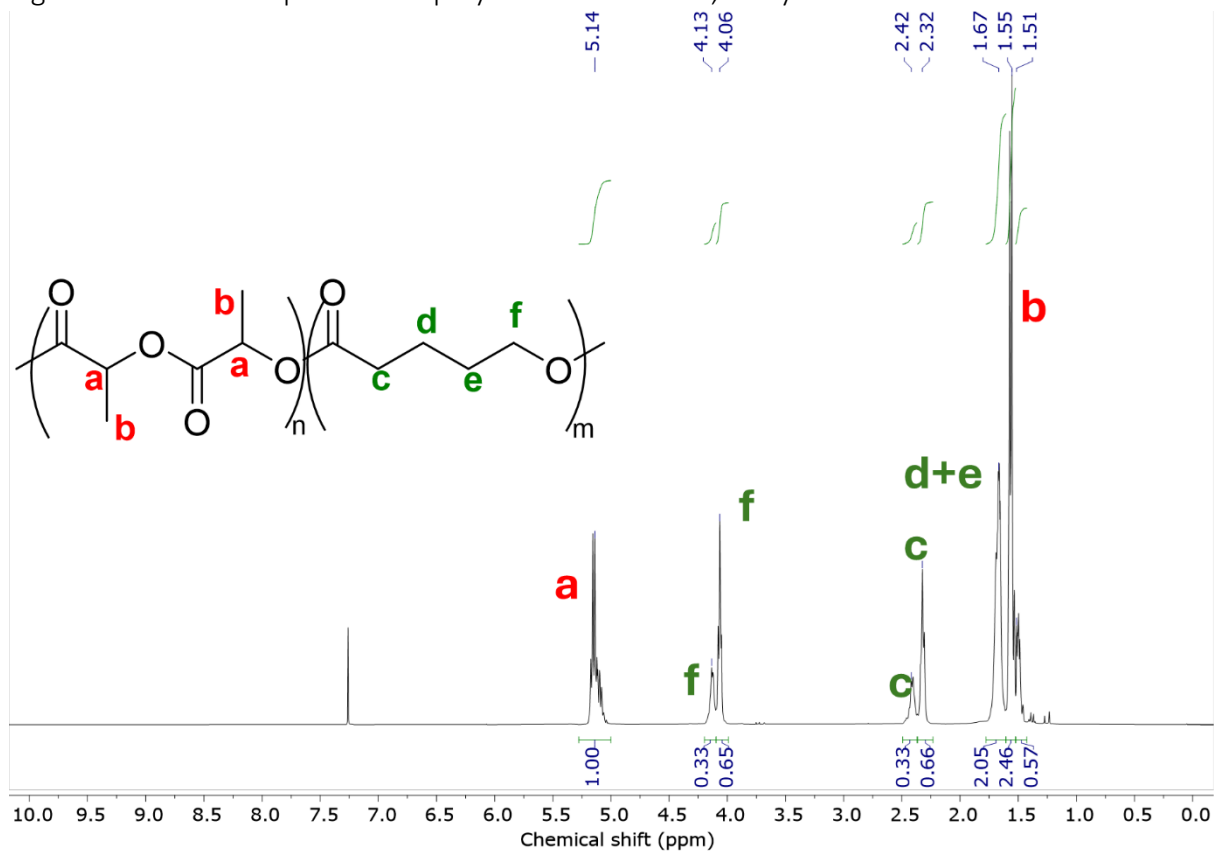


Figure S12: ^1H NMR Spectrum of polymer from Table 2, entry 12

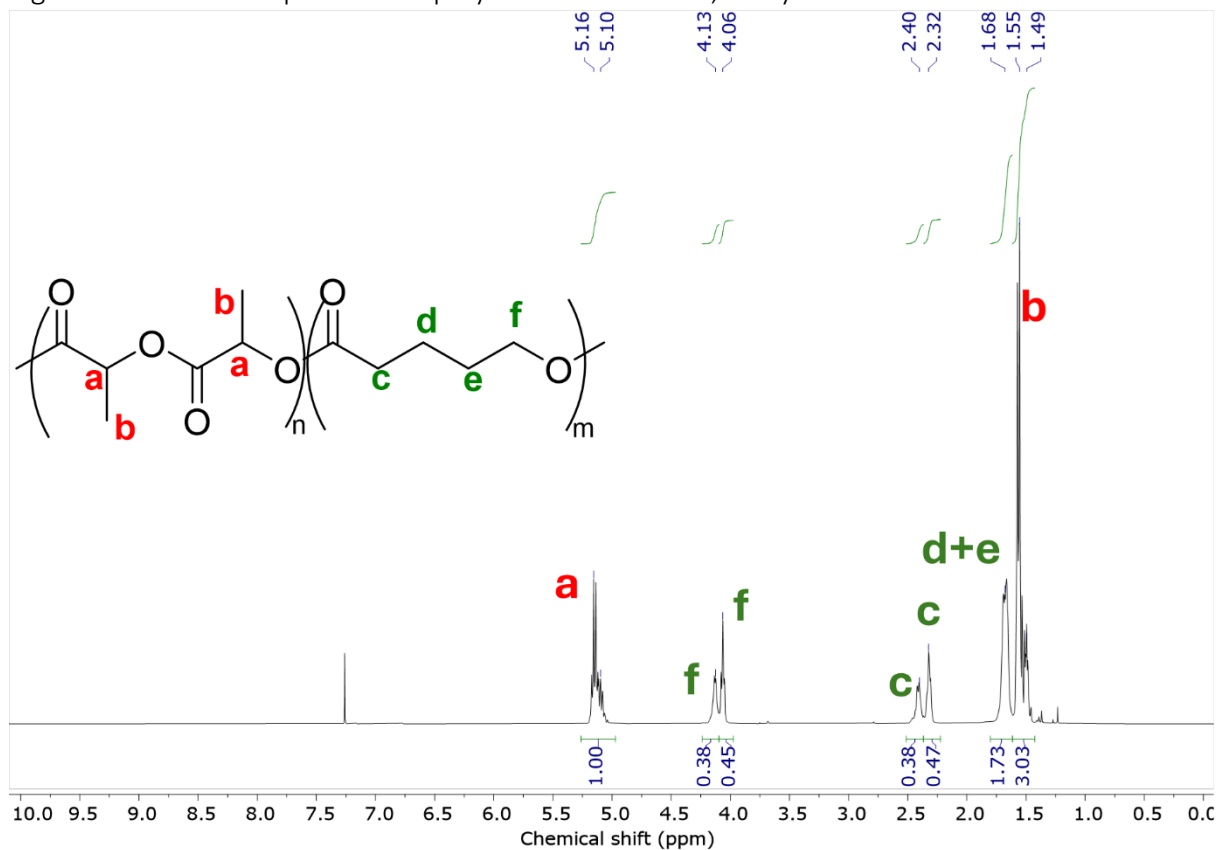


Figure S13: ^{13}C NMR Spectrum of polymer from Table 1, entry 1

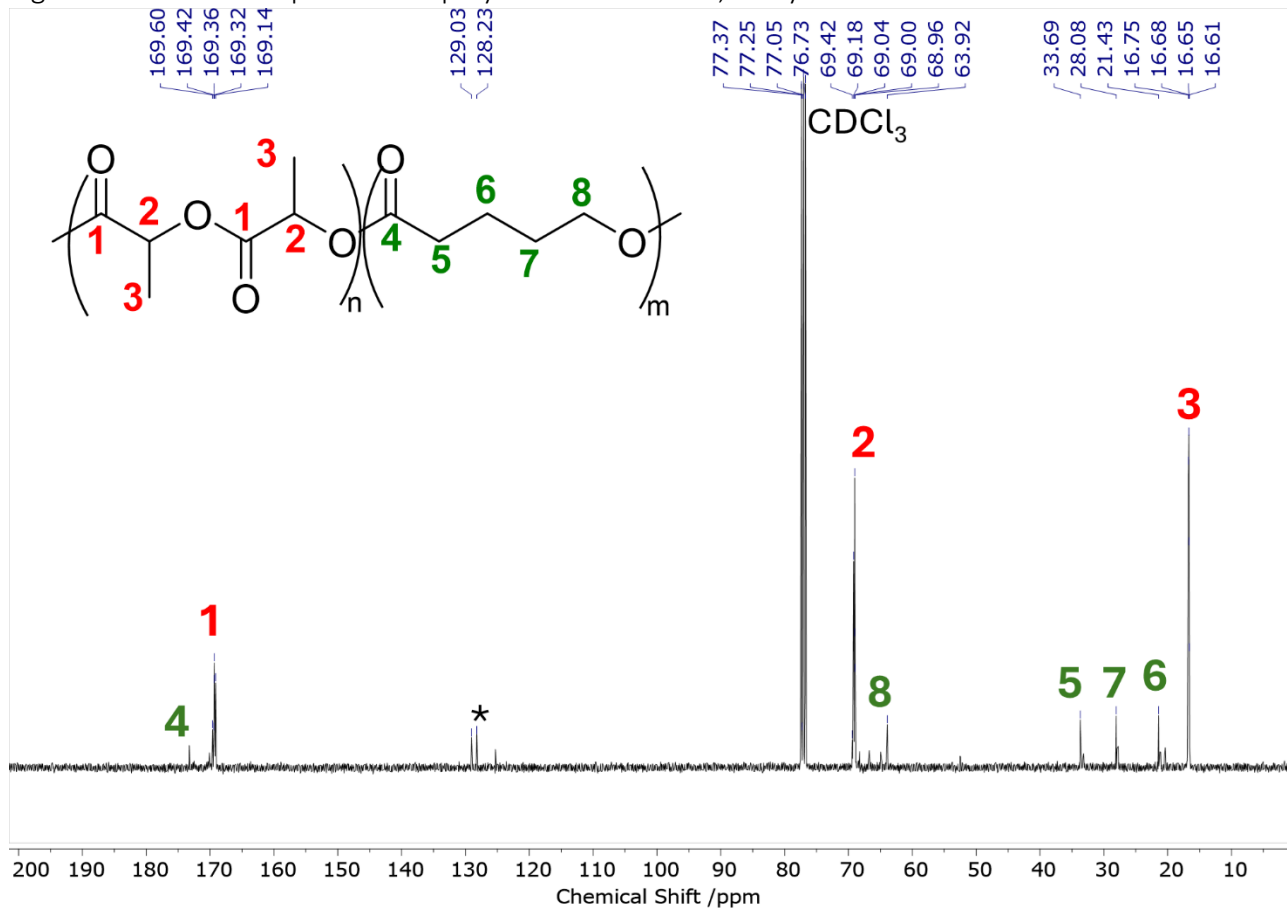


Figure S14: ^{13}C NMR Spectrum of polymer from Table 1, entry 2

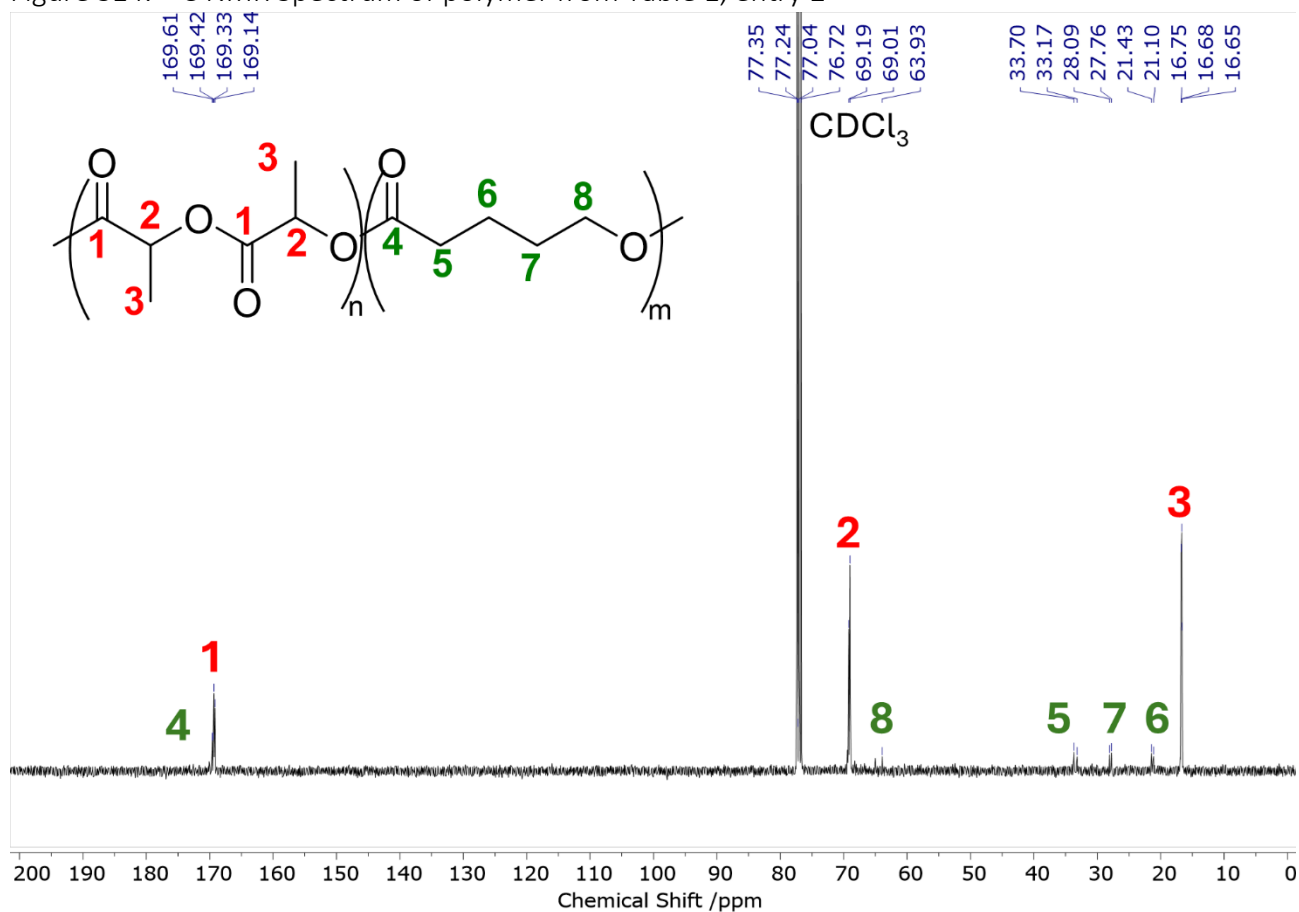


Figure S15: ^{13}C NMR Spectrum of polymer from Table 1, entry 3

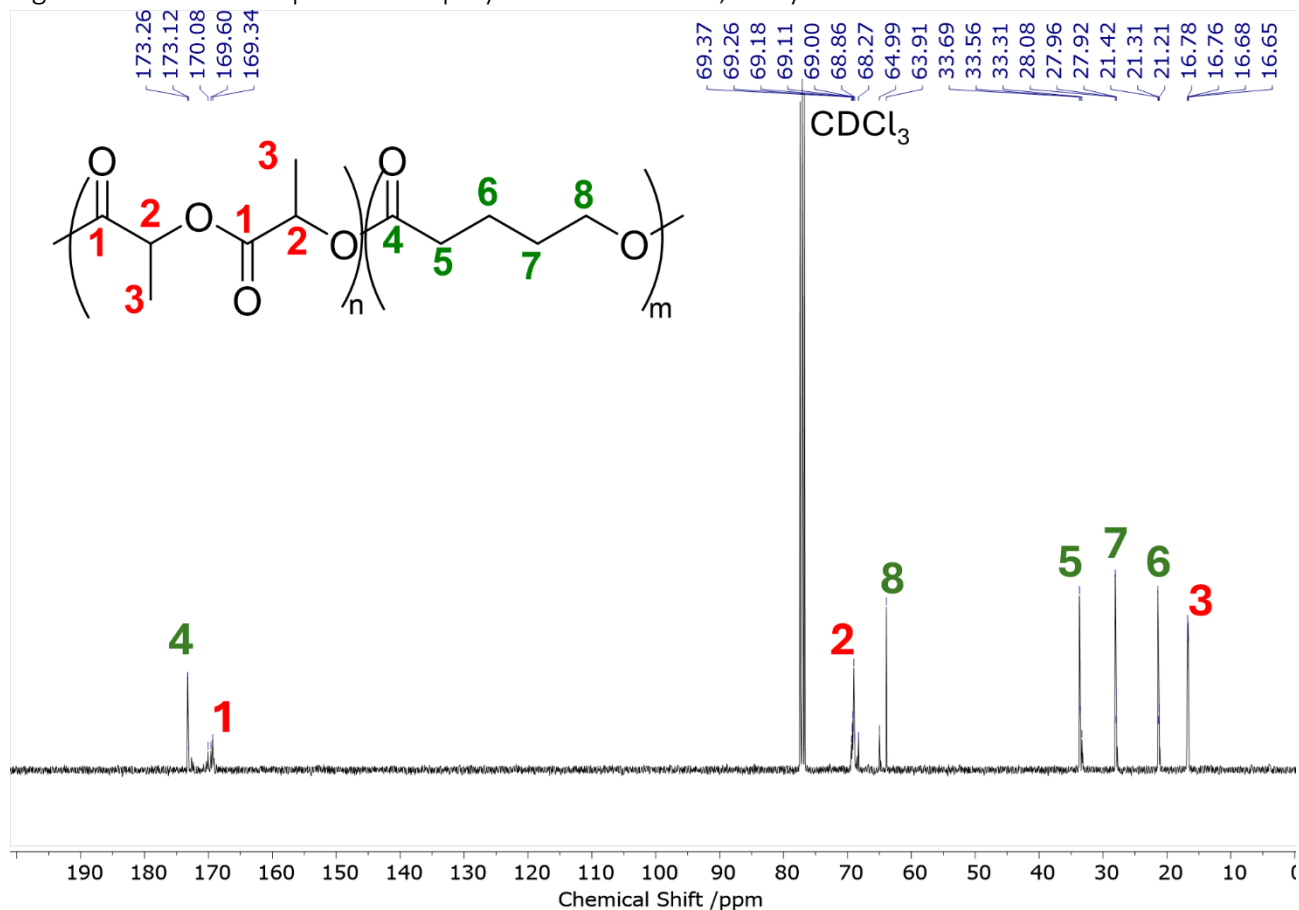


Figure S16: ^{13}C NMR Spectrum of polymer from Table 1, entry 4

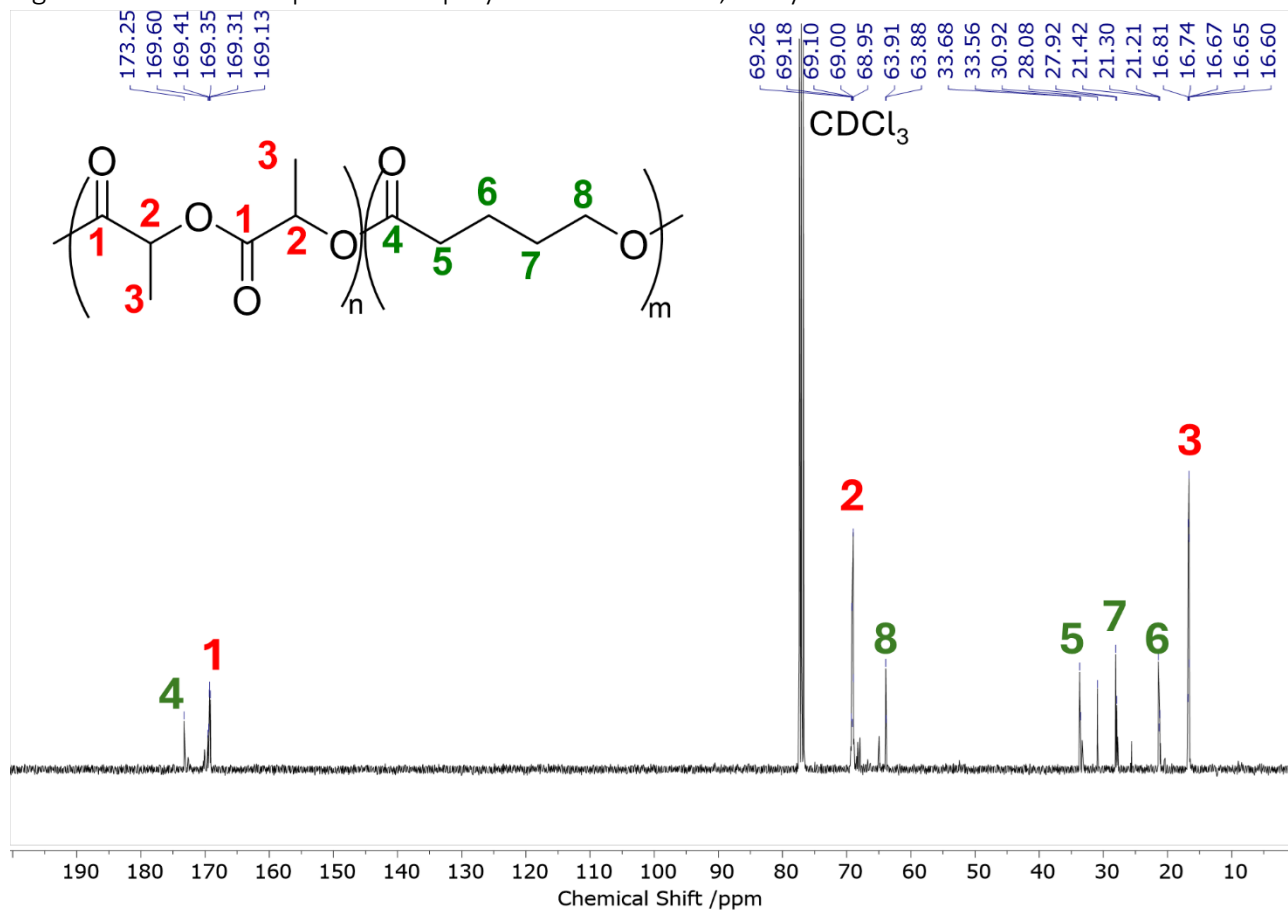


Figure S17: ^{13}C NMR Spectrum of polymer from Table 1, entry 5

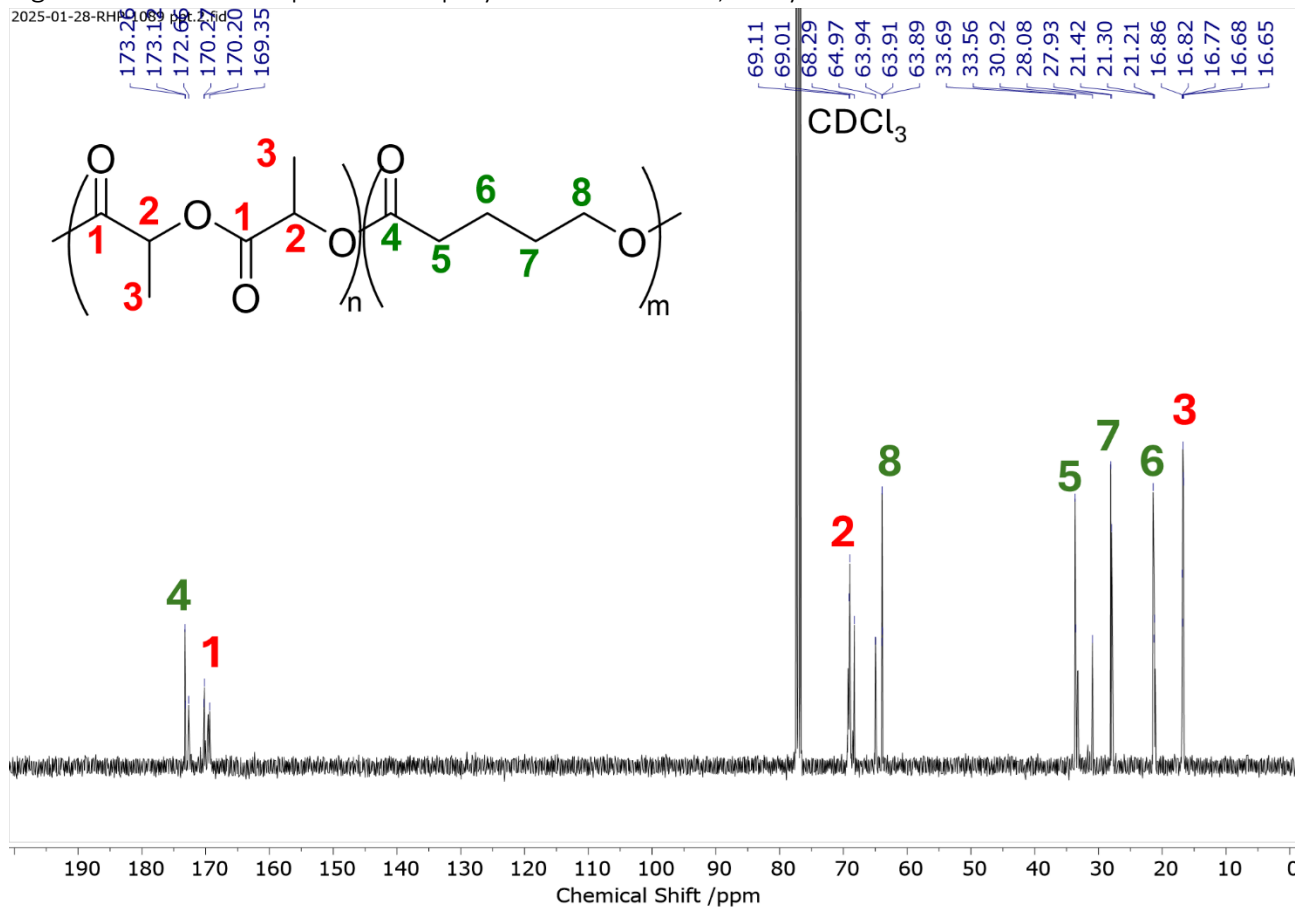


Figure S18: ^{13}C NMR Spectrum of polymer from Table 1, entry 6

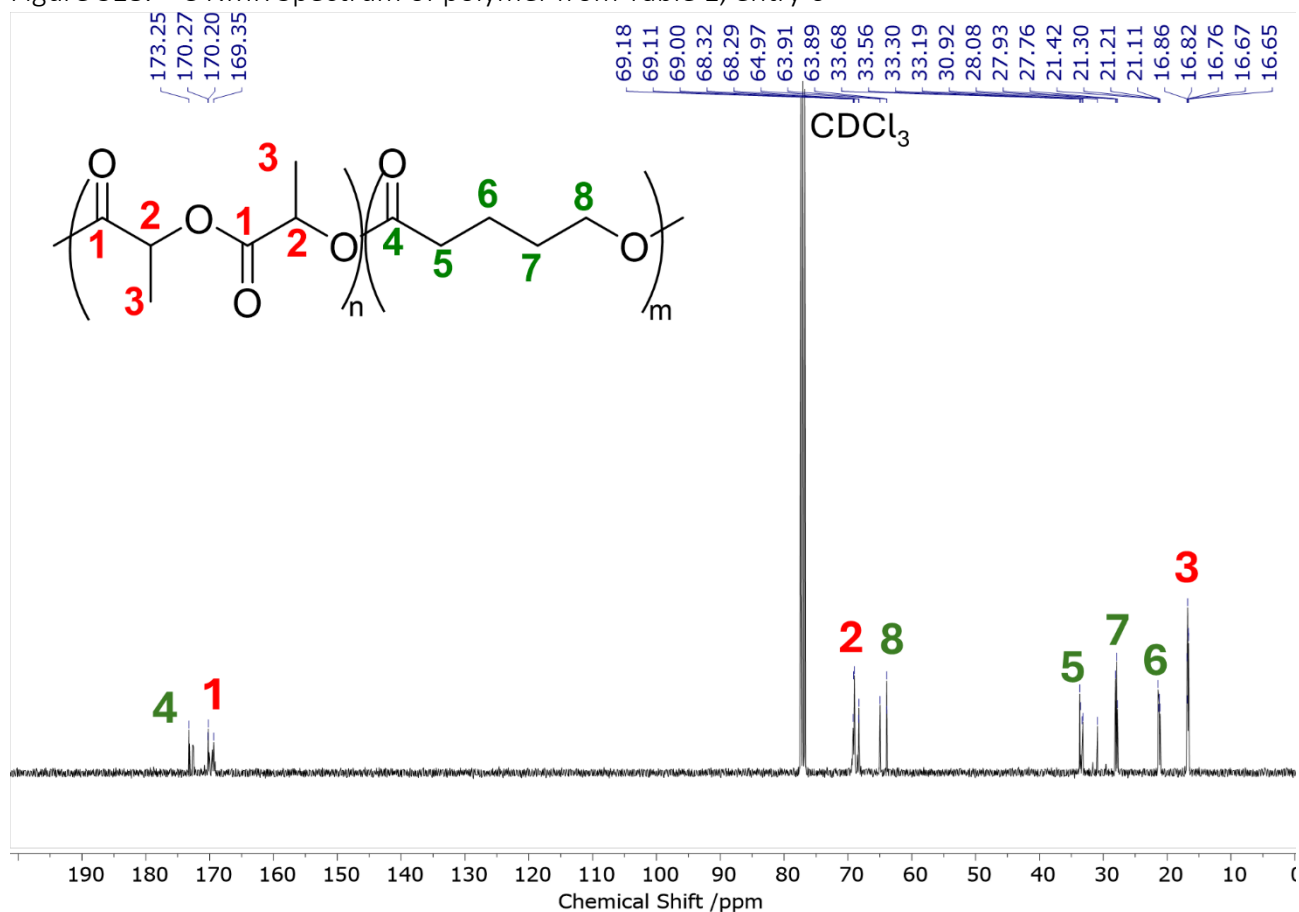


Figure S19: ^{13}C NMR Spectrum of polymer from Table 1, entry 7

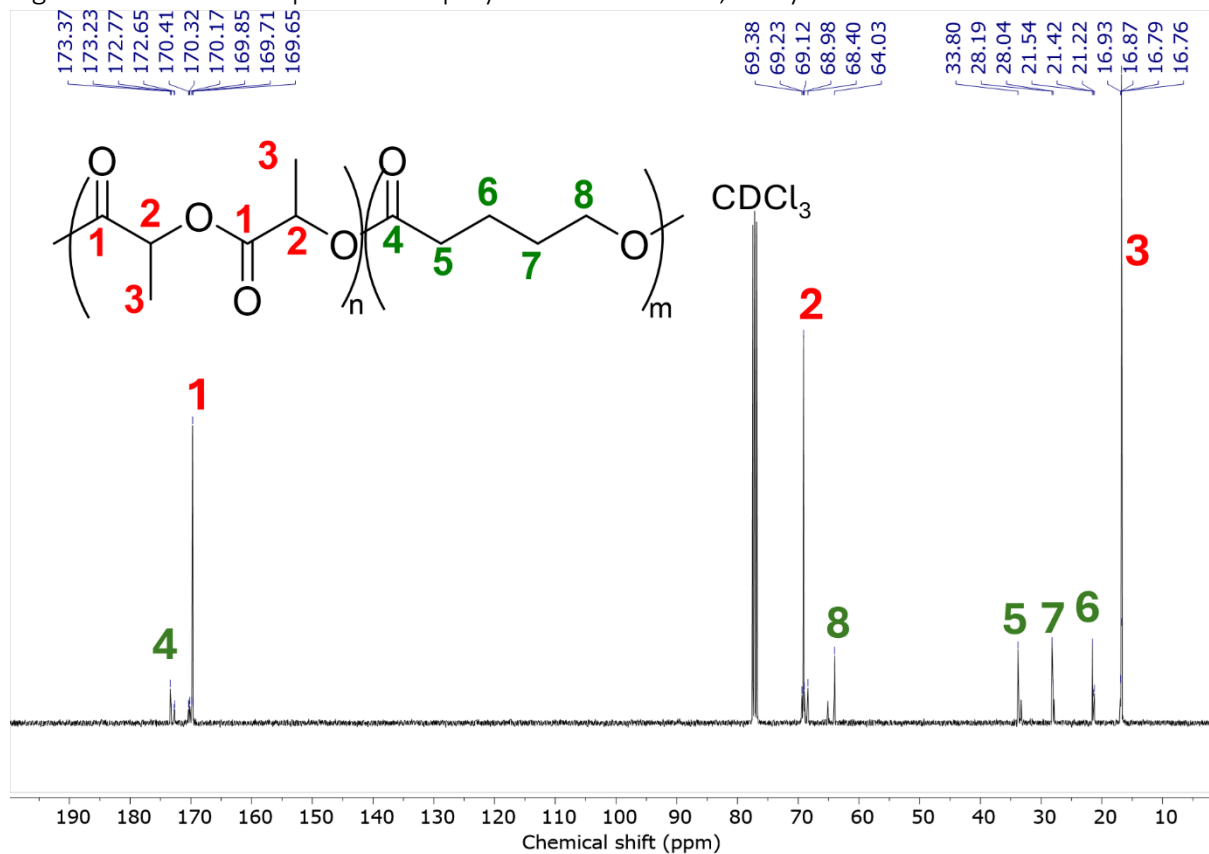


Figure S20: ^{13}C NMR Spectrum of polymer from Table 1, entry 8

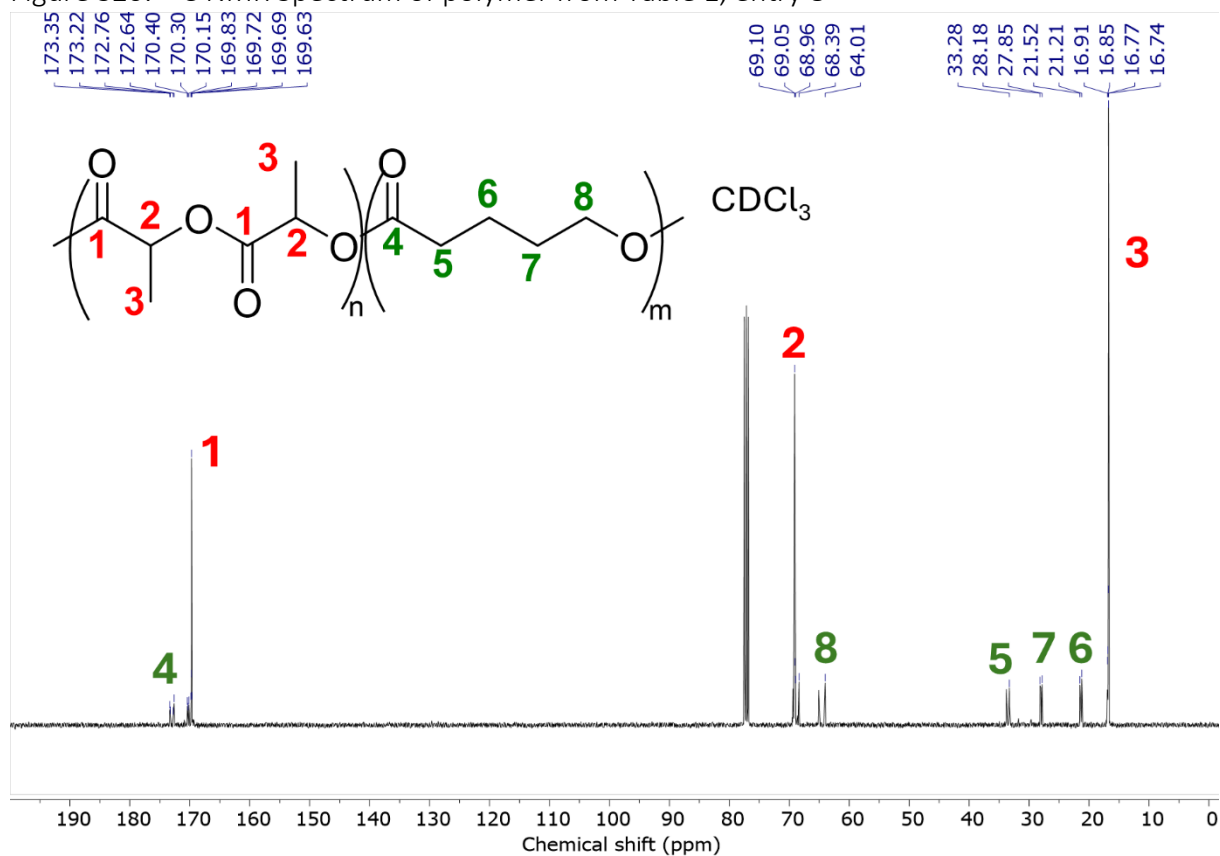


Figure S21: ^{13}C NMR Spectrum of polymer from Table 1, entry 9

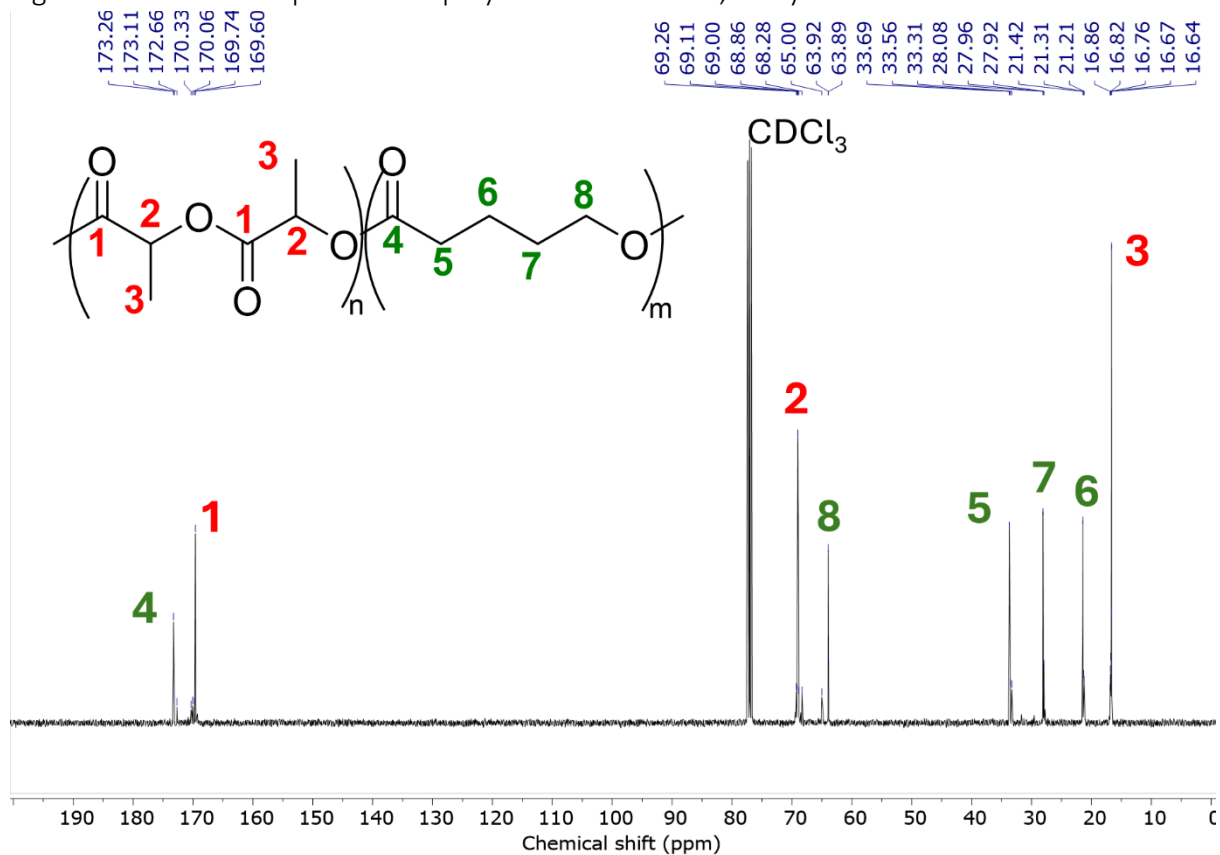


Figure S22: ^{13}C NMR Spectrum of polymer from Table 1, entry 10

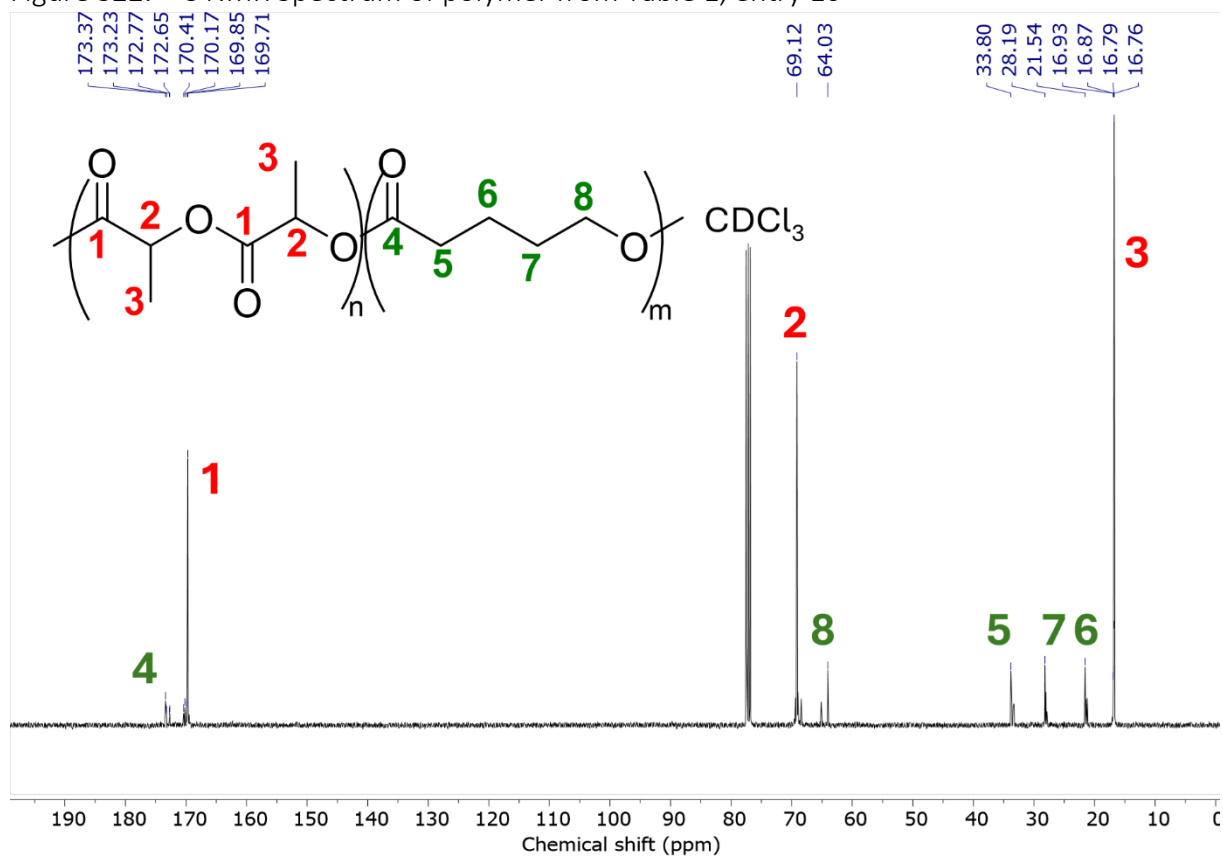
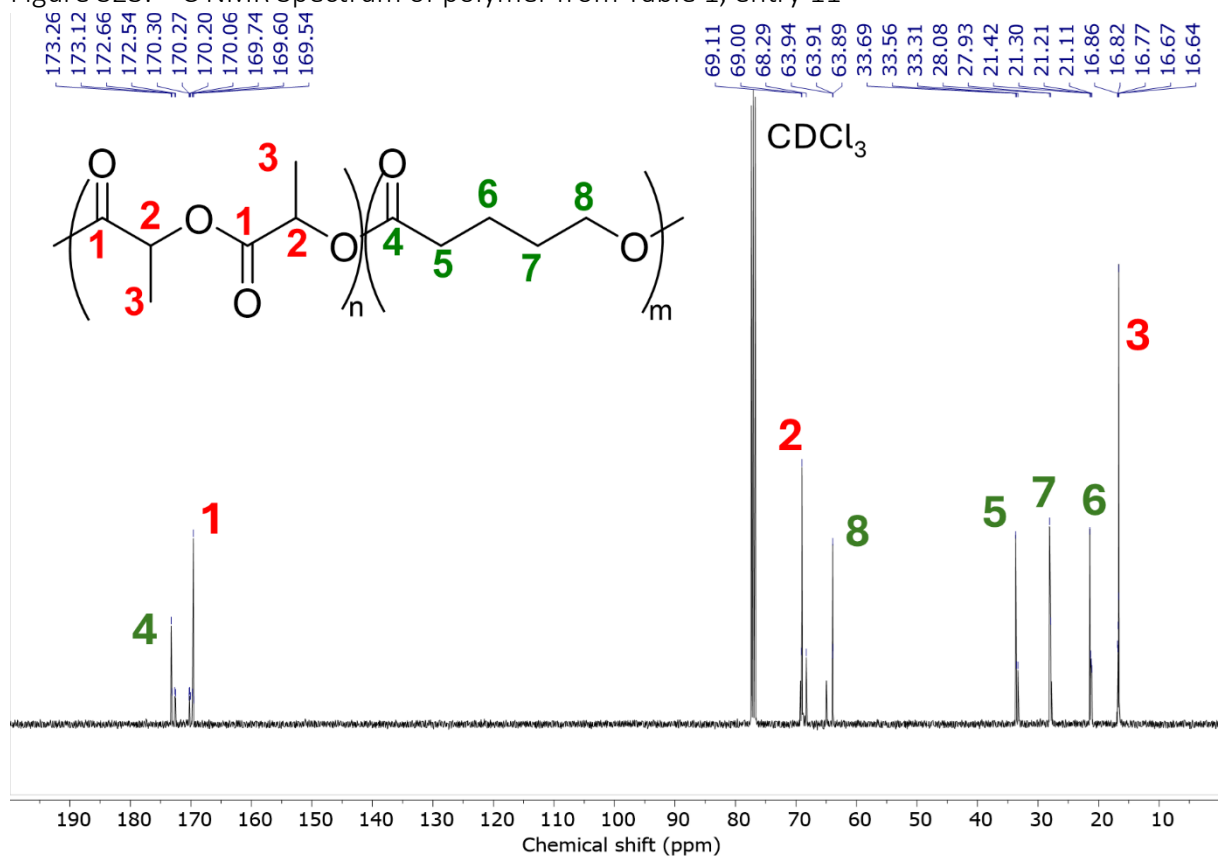


Figure S23: ^{13}C NMR Spectrum of polymer from Table 1, entry 11



Chemical structure of the copolymer: $\text{poly}(\text{2-methyl-2-butenoate-co-2-methyl-3-pentenoate})$. The structure shows two repeating units: a 2-methyl-2-butenoate unit (labeled with red numbers 1-3) and a 2-methyl-3-pentenoate unit (labeled with green numbers 4-8). The units are connected by ester linkages.

^{13}C NMR spectrum (CDCl₃) showing chemical shifts (ppm) for the copolymer. The spectrum displays peaks corresponding to the labeled carbons in the structure.

Chemical shifts (ppm) for the labeled carbons:

- Red numbers (1-3): 173.36, 173.22, 172.76, 172.64, 170.37, 170.34, 170.31, 170.16, 169.84, 169.70, 169.64.
- Green numbers (4-8): 69.36, 69.21, 69.11, 68.42, 68.39, 65.07, 65.05, 64.04, 64.02, 63.99, 33.79, 33.67, 33.41, 33.29, 28.18, 28.03, 27.87, 21.53, 21.40, 21.32, 21.21, 16.96, 16.92, 16.87, 16.78, 16.74.

Chemical shift (ppm) for the solvent (CDCl₃): 77.0 ppm.

173.26
173.12
170.08
169.60
169.34

VVV
LLVV
VVLL
LLVLL
LLLLV
VLV
VLLV
VLLV
VLLL
LLLLV
LLLLL
VLLL

Chemical Shift /ppm

2025-01-28-RHP-1089 ppt.2.fid



Figure S28: Carbonyl region of the ^{13}C NMR Spectrum of polymer from Table 1, entry 7

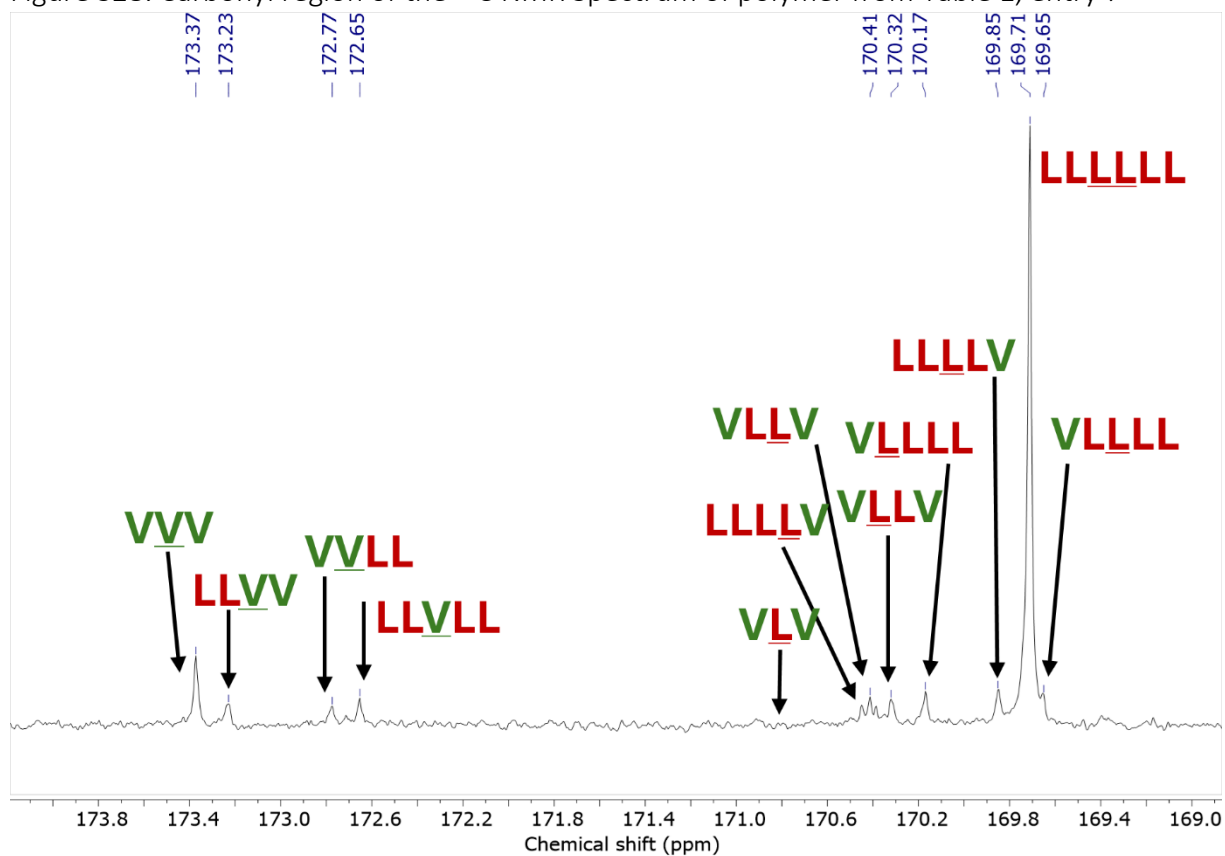


Figure S29: Carbonyl region of the ^{13}C NMR Spectrum of polymer from Table 1, entry 8

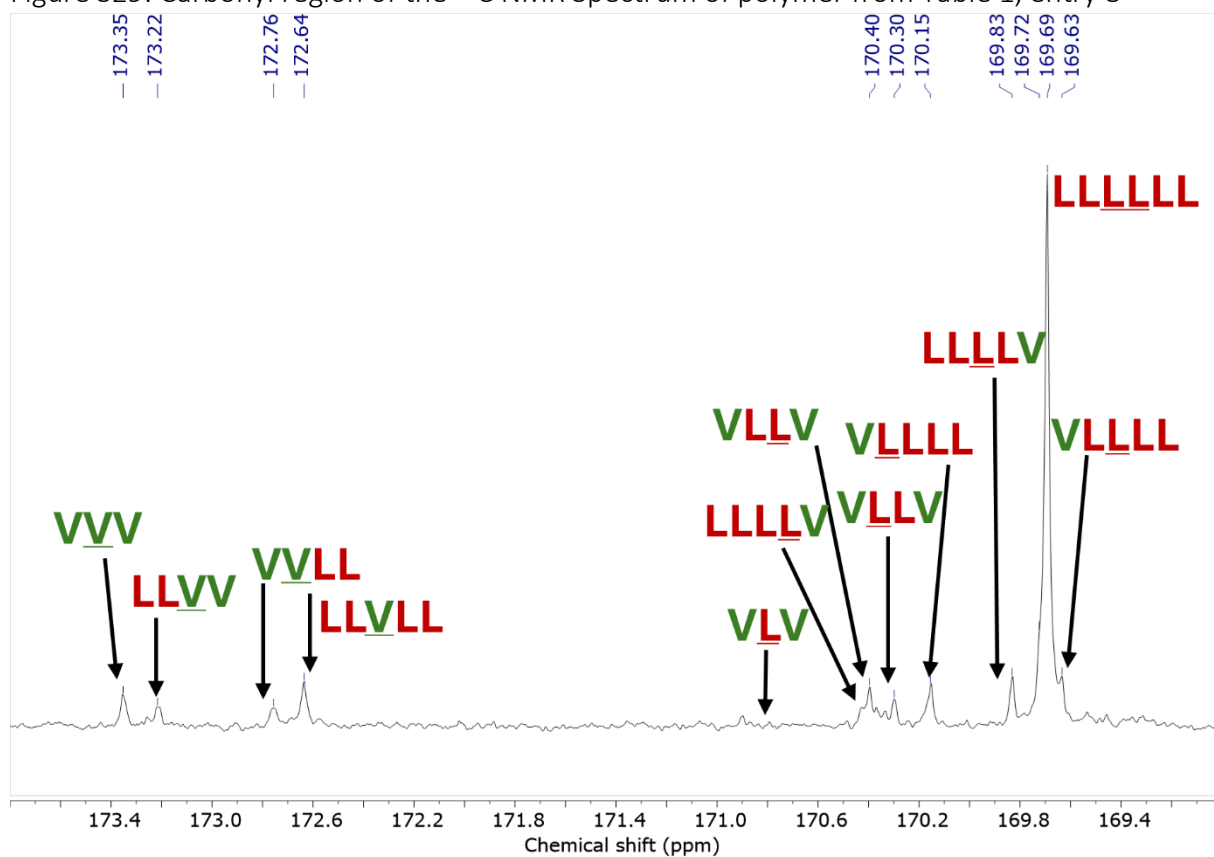


Figure S30: Carbonyl region of the ^{13}C NMR Spectrum of polymer from Table 1, entry 9

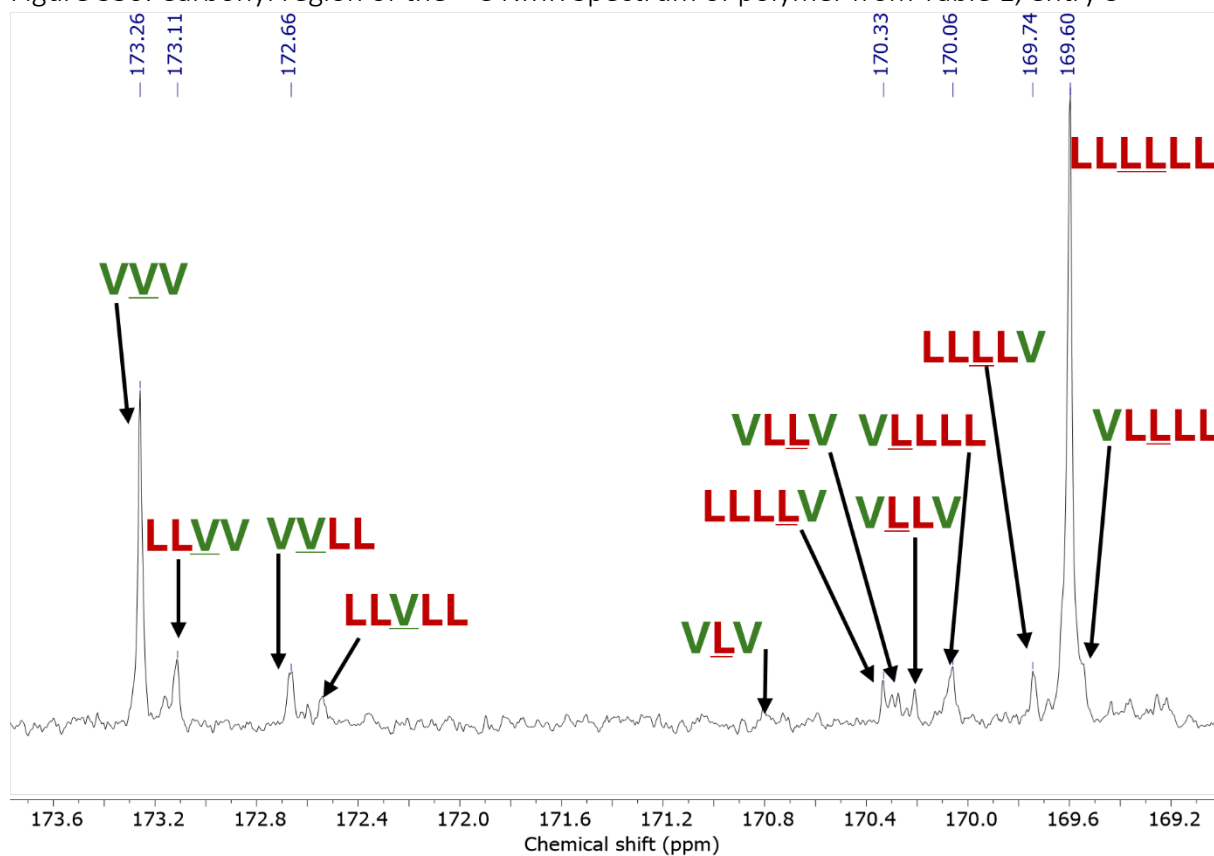


Figure S31: Carbonyl region of the ^{13}C NMR Spectrum of polymer from Table 1, entry 10

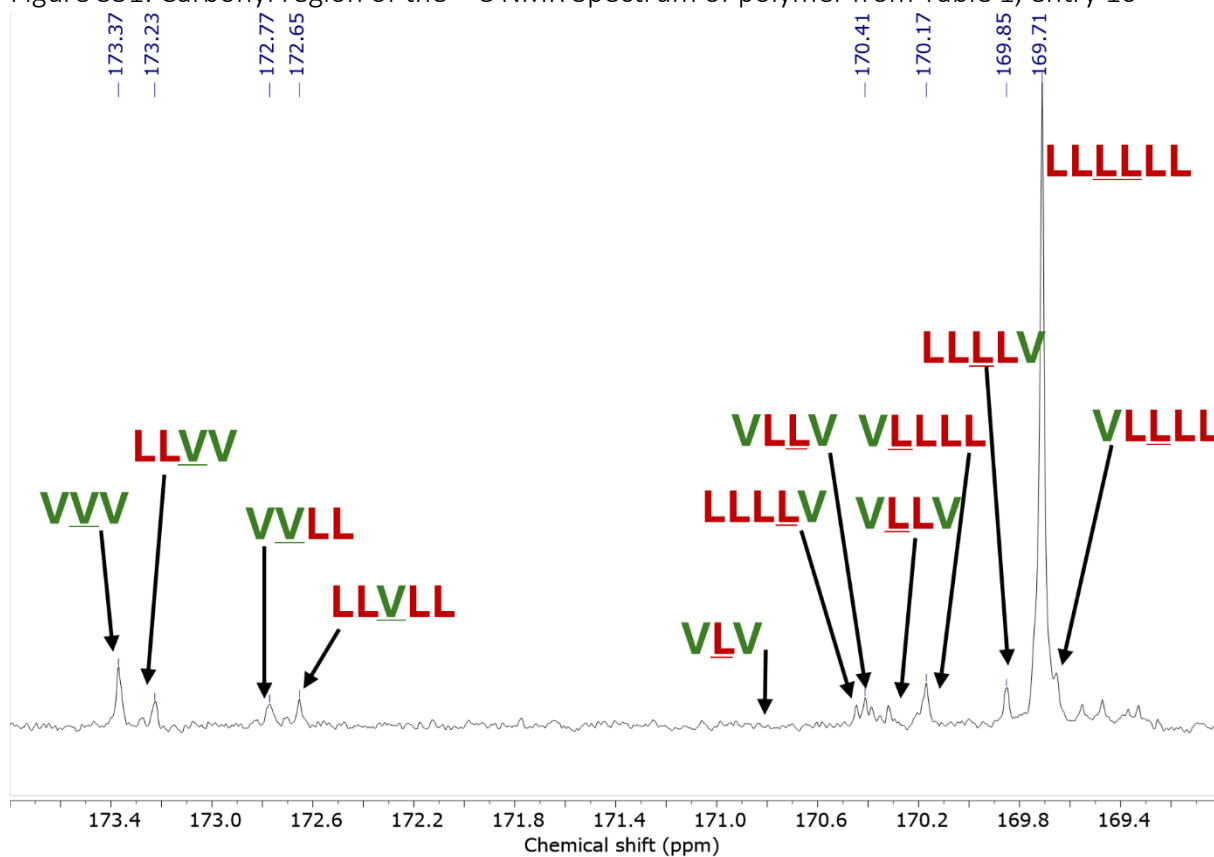


Figure S30: Carbonyl region of the ^{13}C NMR Spectrum of polymer from Table 1, entry 11

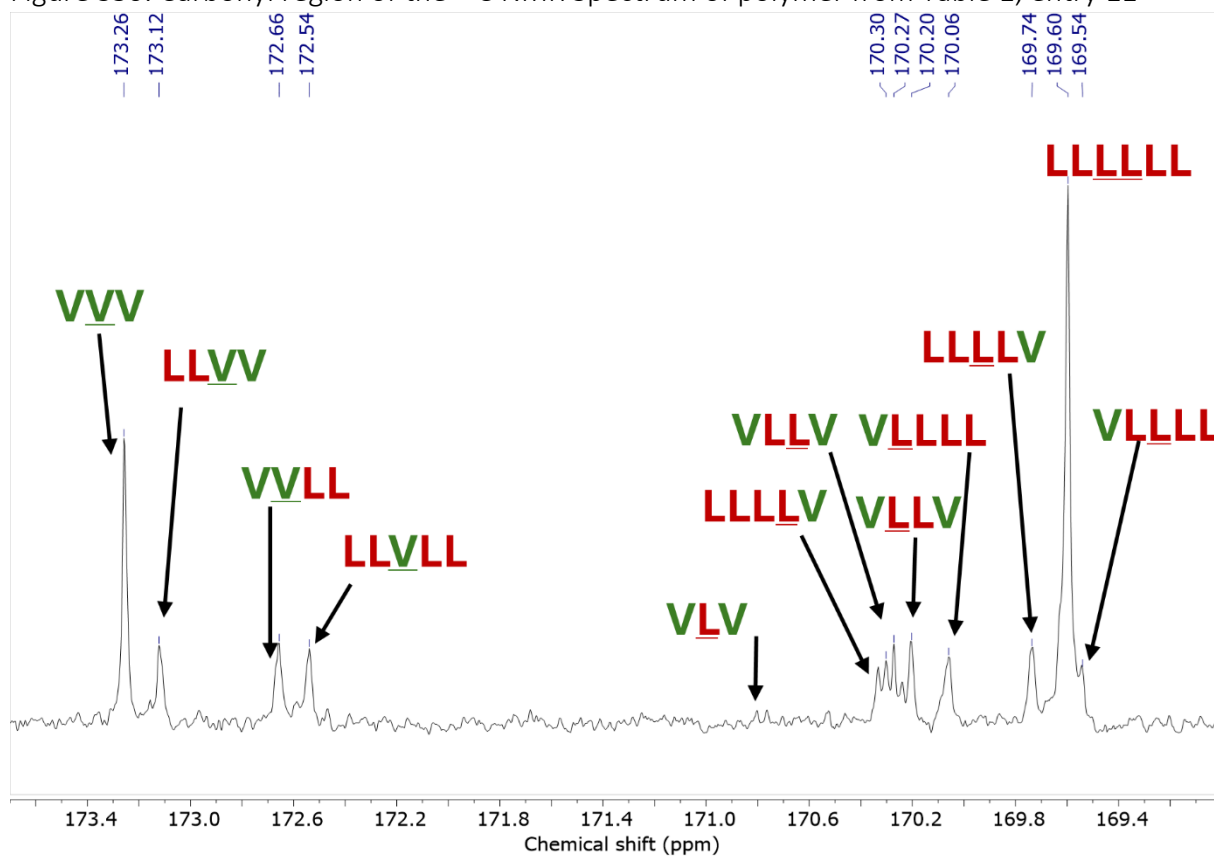


Figure S31: Carbonyl region of the ^{13}C NMR Spectrum of polymer from Table 1, entry 12

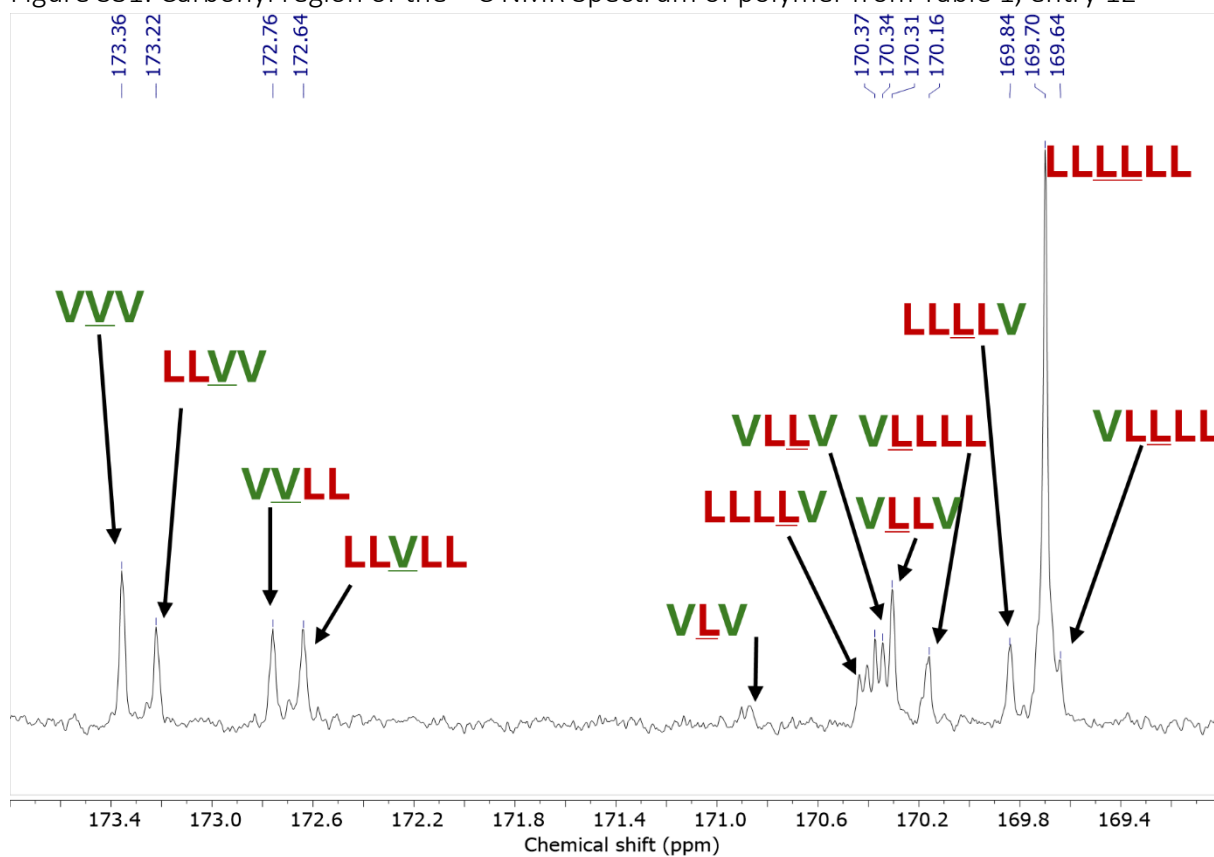


Figure S32: ^1H NMR Spectrum of polymer from Table 3, entry 1

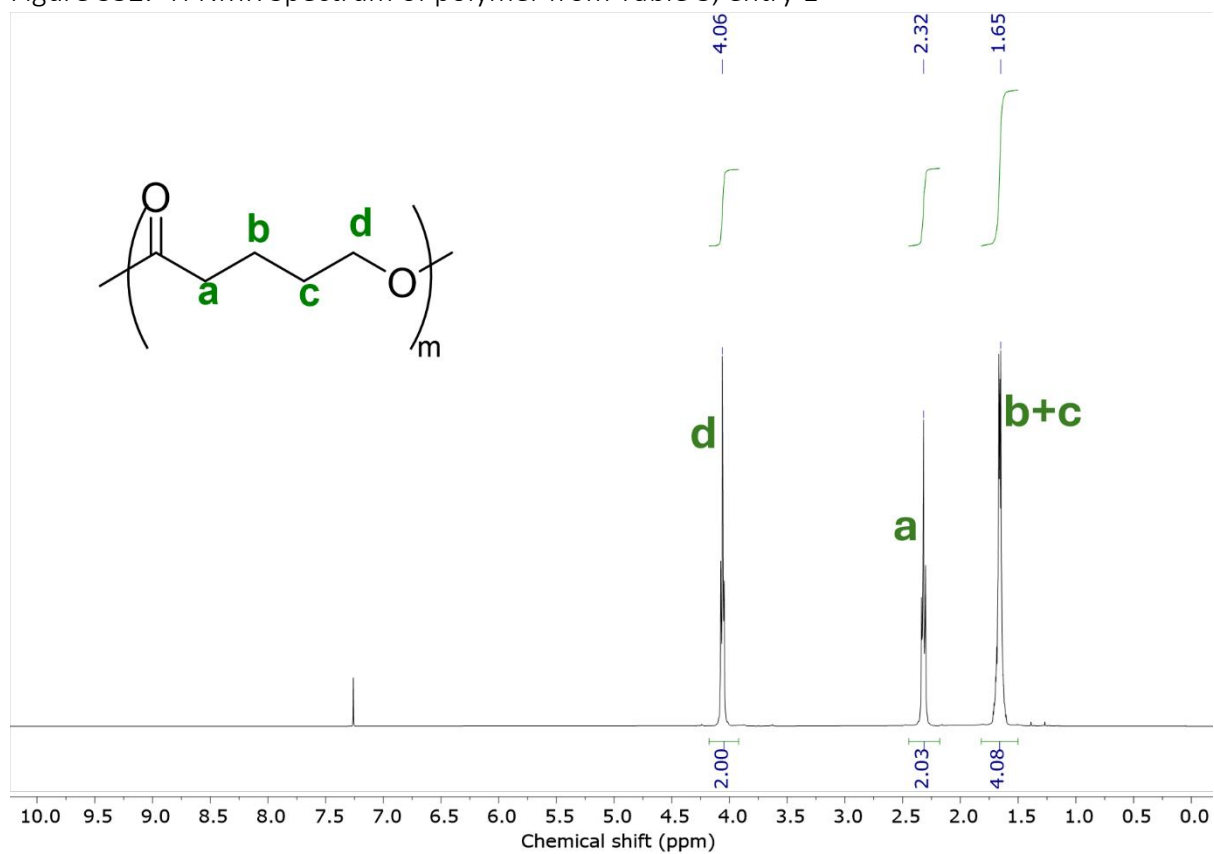


Figure S33: ^1H NMR Spectrum of polymer from Table 3, entry 2

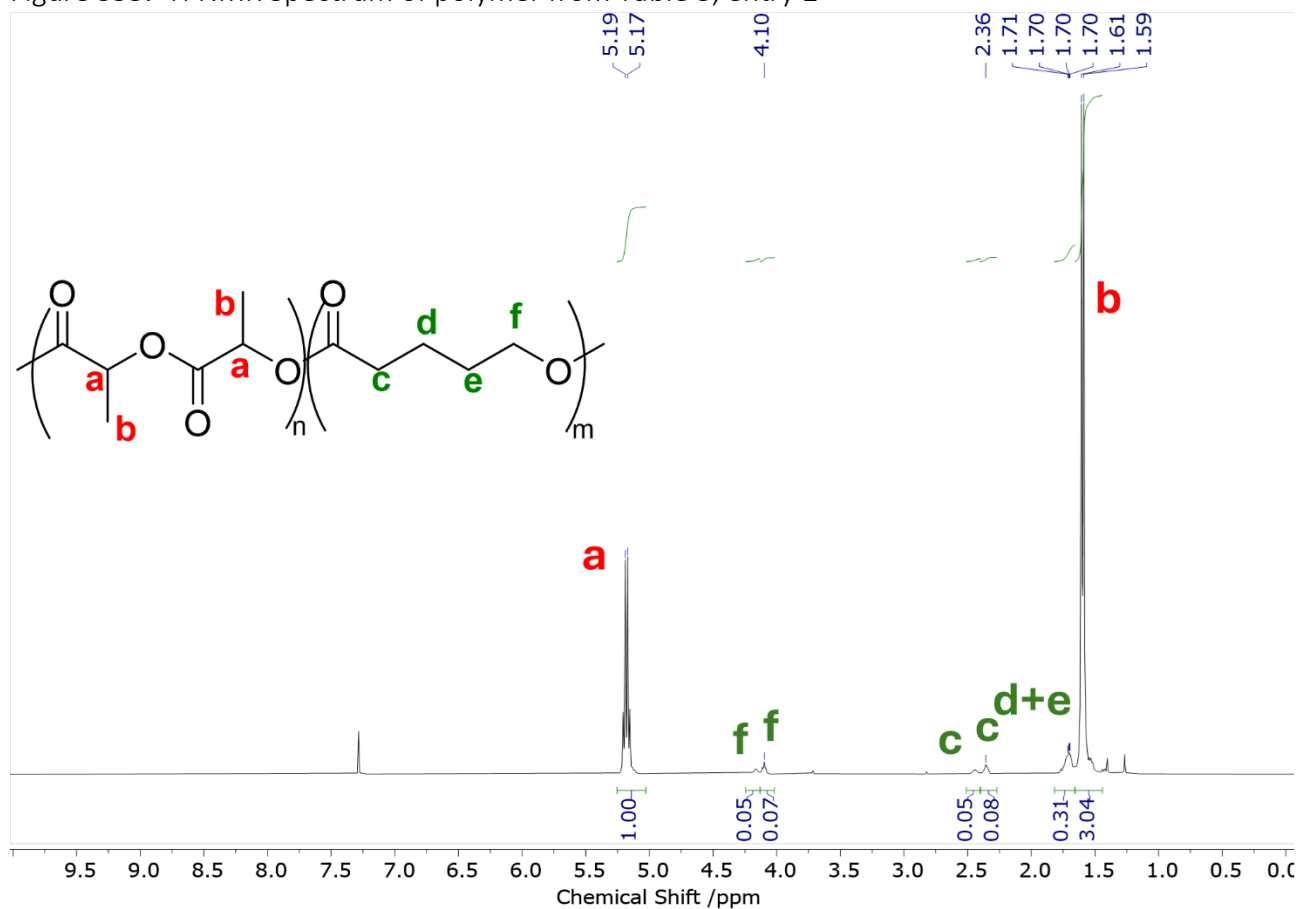


Figure S34: ^1H NMR Spectrum of polymer from Table 3, entry 3

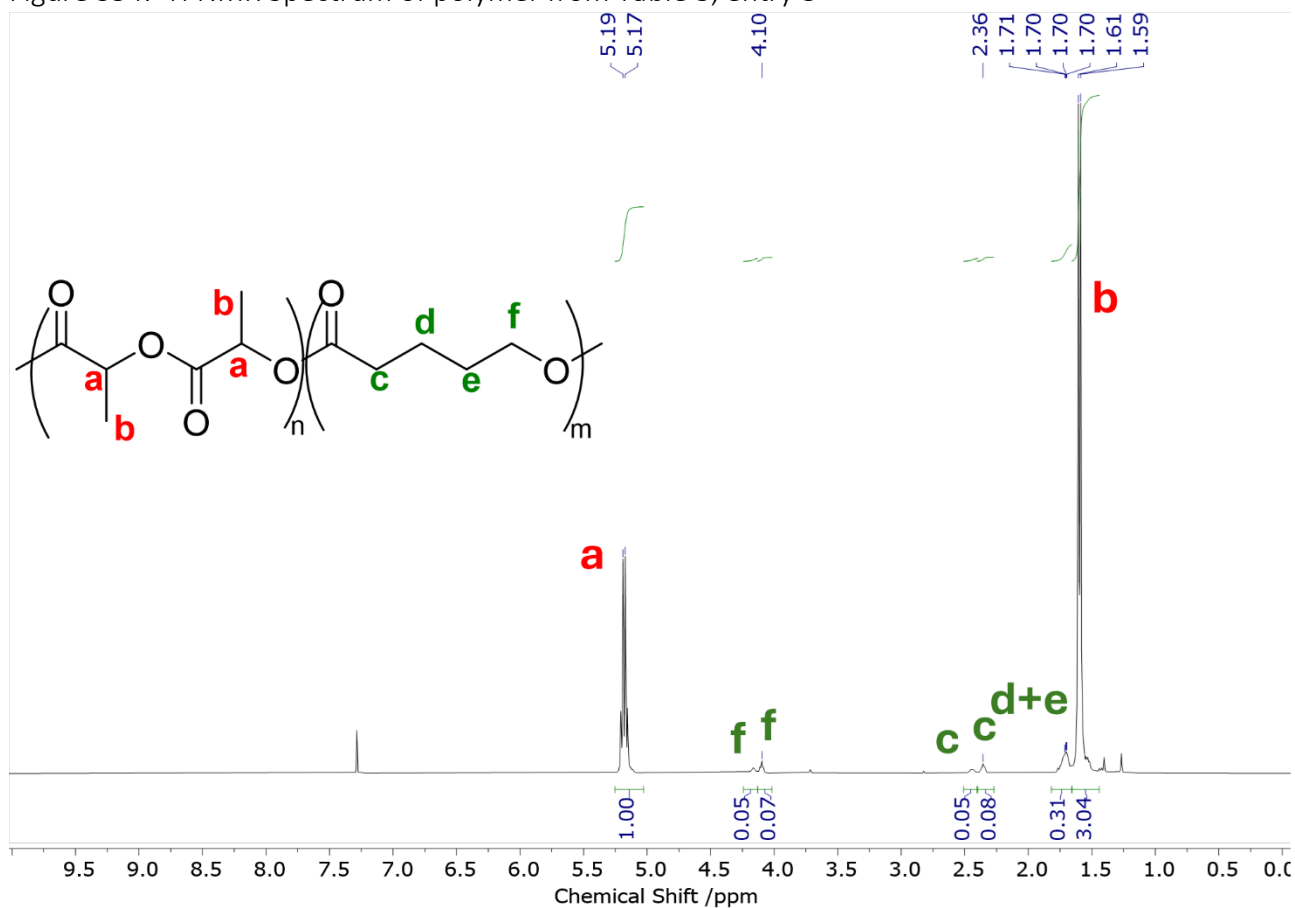


Figure S35: ^1H NMR Spectrum of polymer from Table 3, entry 4

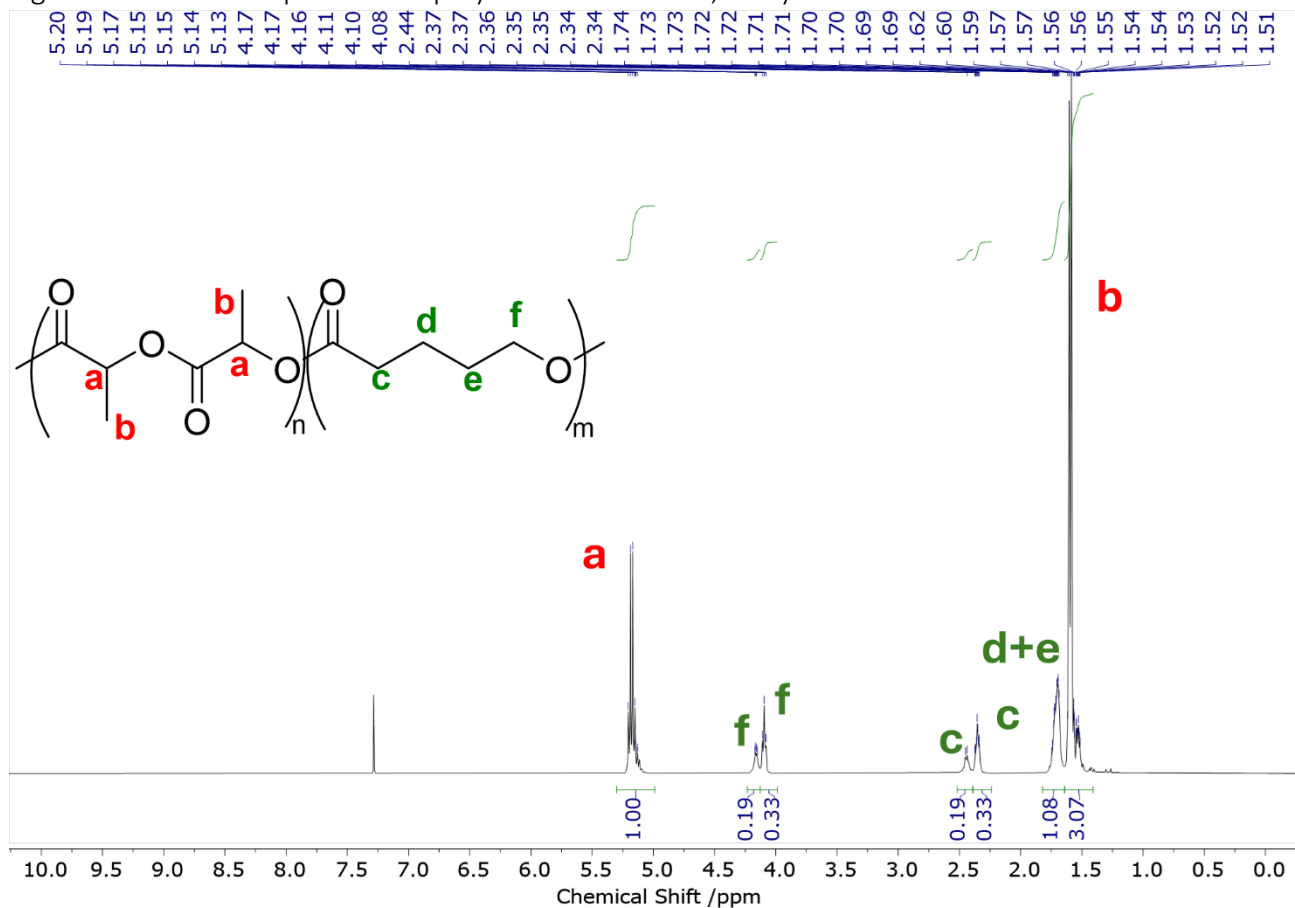


Figure S36: ^1H NMR Spectrum of polymer from Table 3, entry 5

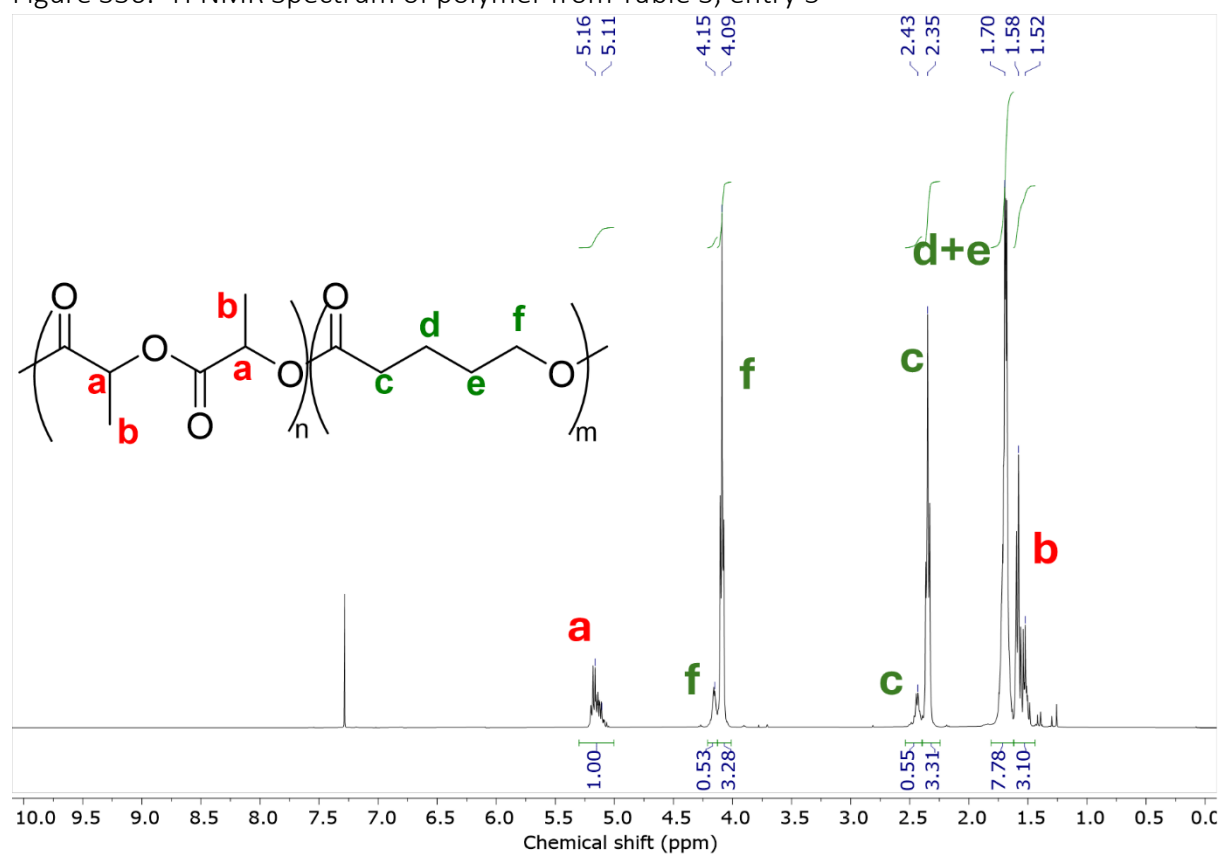


Figure S37: ^{13}C NMR Spectrum of polymer from Table 2, entry 1

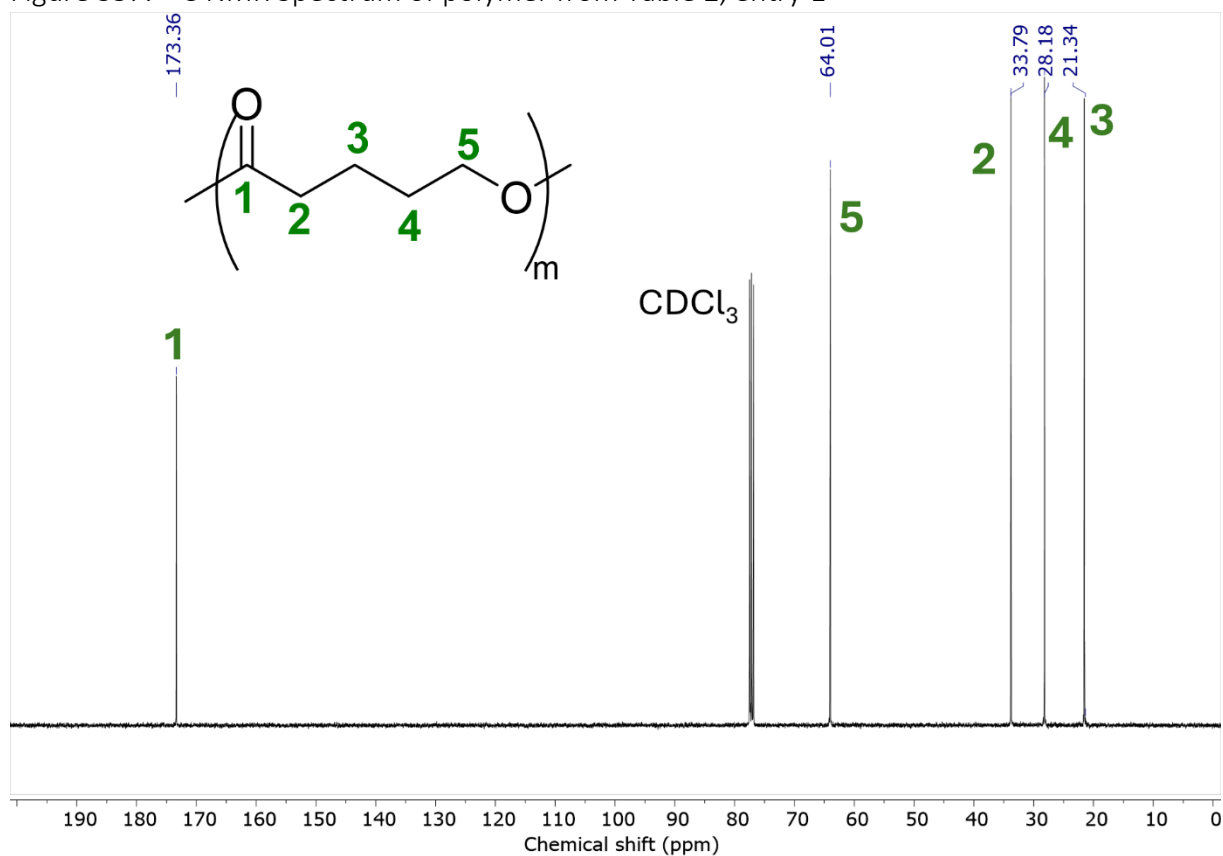


Figure S38: ^{13}C NMR Spectrum of polymer from Table 2, entry 2

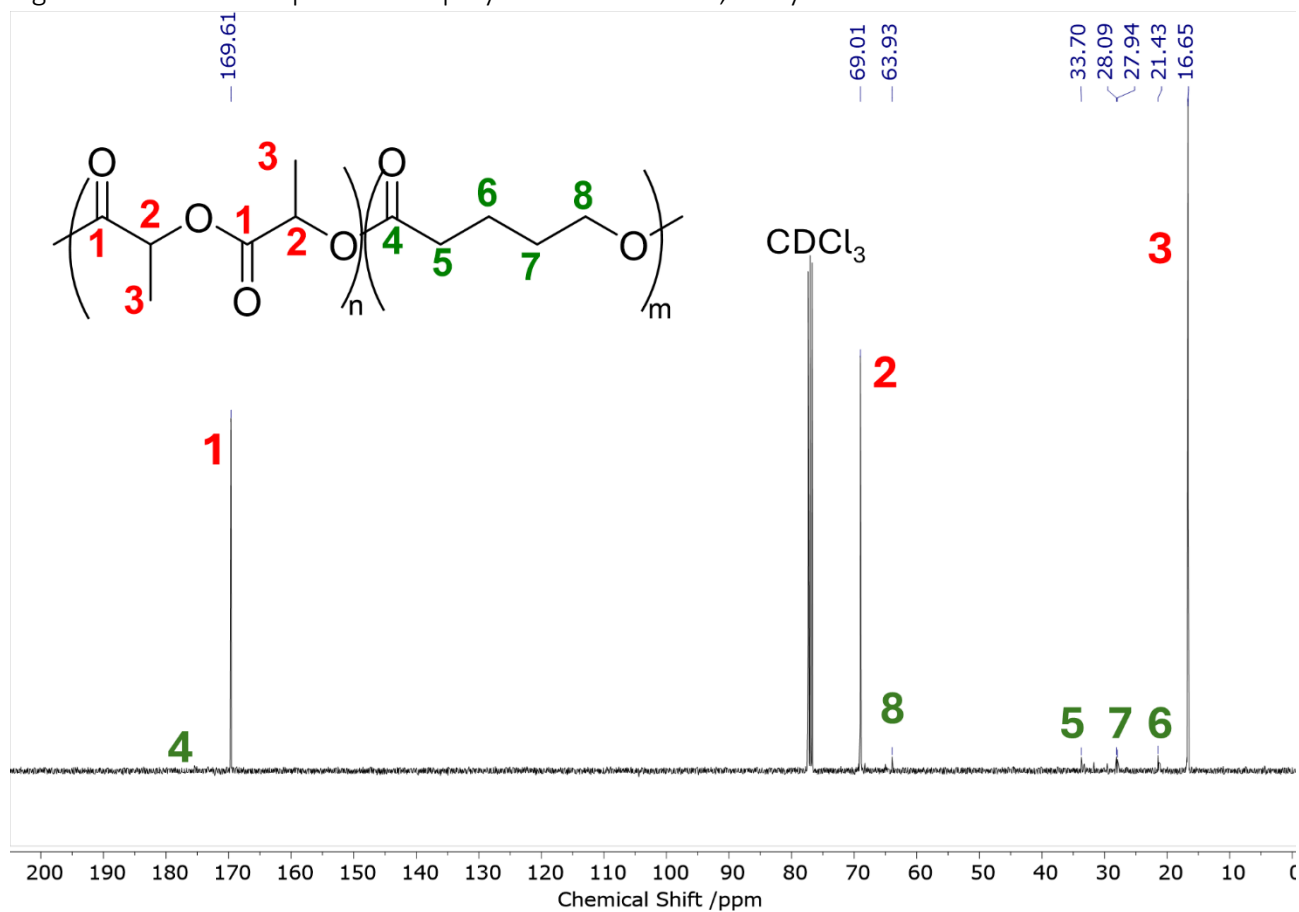


Figure S39: ^{13}C NMR Spectrum of polymer from Table 2, entry 3

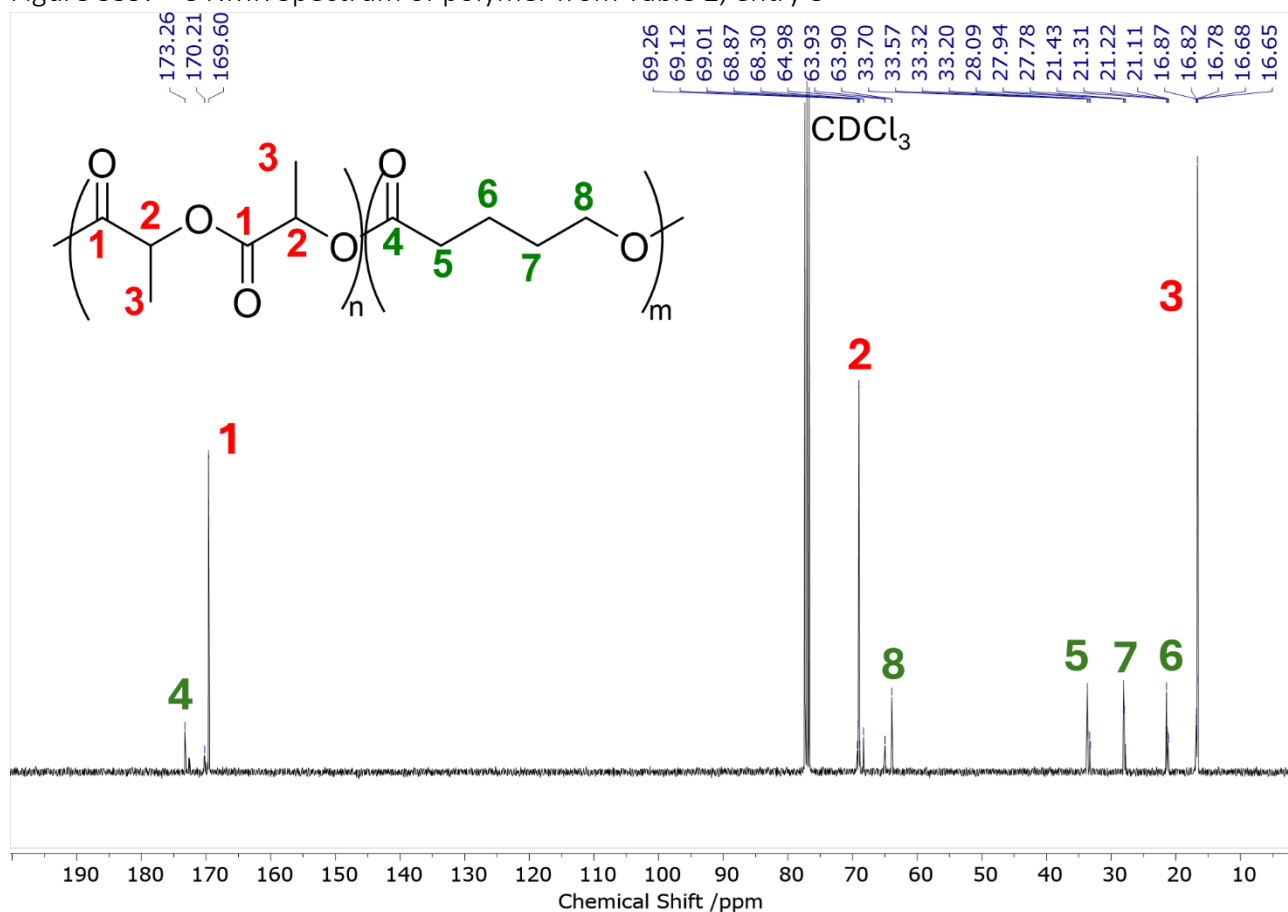


Figure S40: ^{13}C NMR Spectrum of polymer from Table 2, entry 4

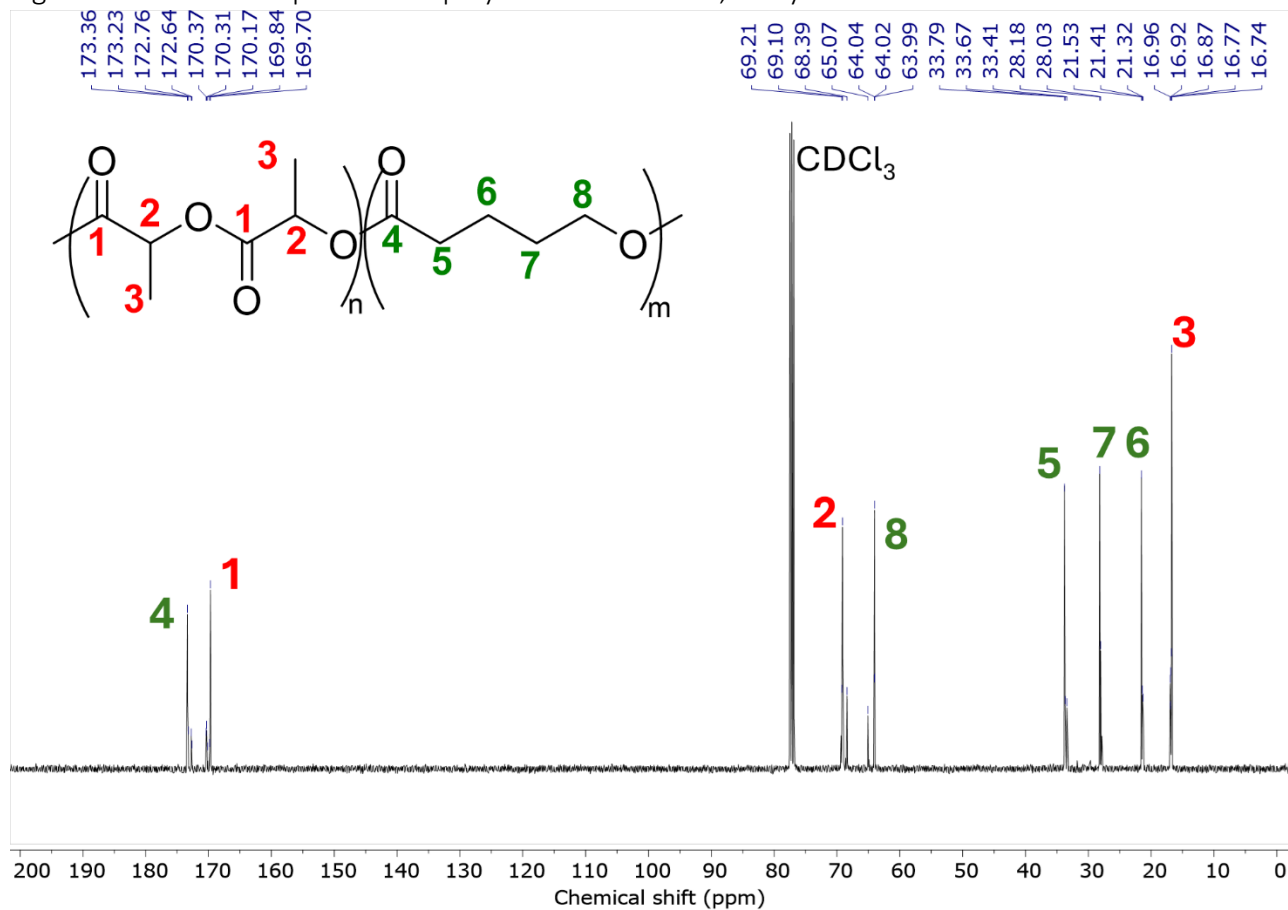


Figure S41: ^{13}C NMR Spectrum of polymer from Table 2, entry 5

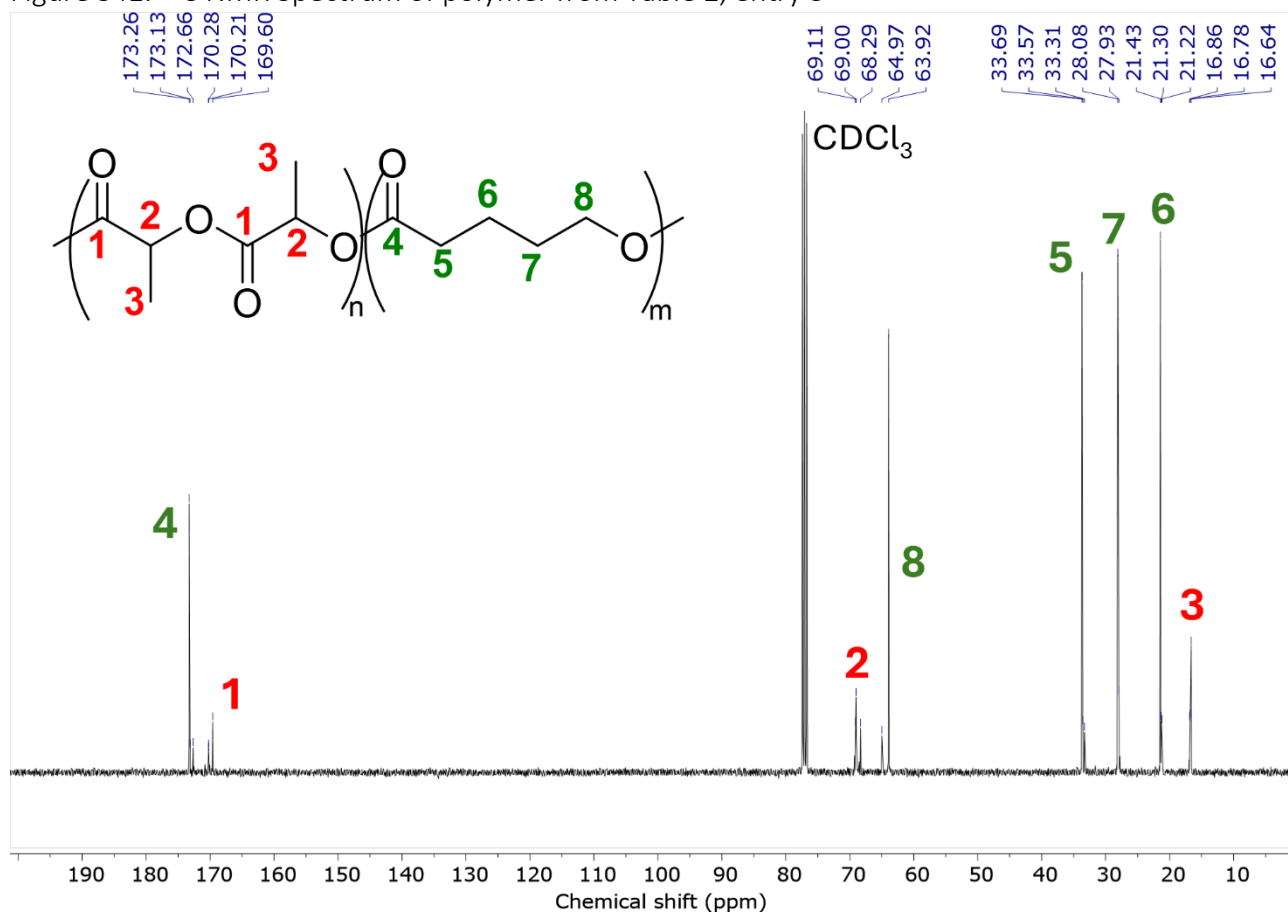
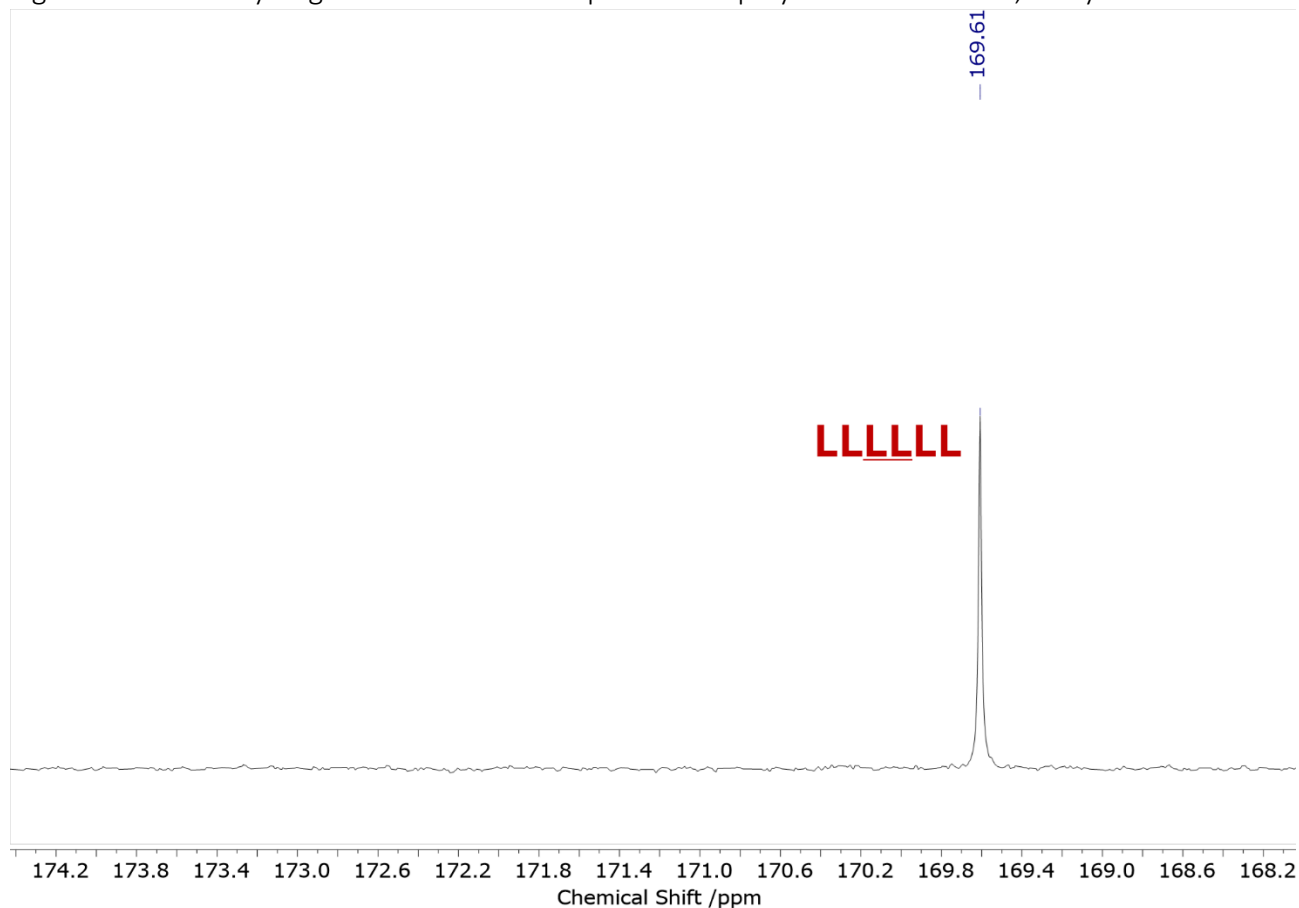


Figure S42: Carbonyl region of the ^{13}C NMR Spectrum of polymer from Table 2, entry 2



The figure displays a ^{13}C NMR spectrum of poly(L-leucine). The x-axis represents the chemical shift in ppm, ranging from 168.8 to 173.6. Several peaks are identified and labeled with sequences representing different carbon environments in the polymer chain:

- VVV**: Peak at approximately 173.26 ppm.
- LLVV**: Peak at approximately 173.13 ppm.
- VVLL**: Peak at approximately 172.67 ppm.
- LLVLL**: Peak at approximately 172.55 ppm.
- VLV**: Peak at approximately 170.21 ppm.
- LLLL**: Peak at approximately 170.0 ppm.
- VLLV**: Peak at approximately 170.0 ppm.
- VLLL**: Peak at approximately 170.0 ppm.
- LLLL**: Peak at approximately 169.60 ppm.
- VLLL**: Peak at approximately 169.60 ppm.

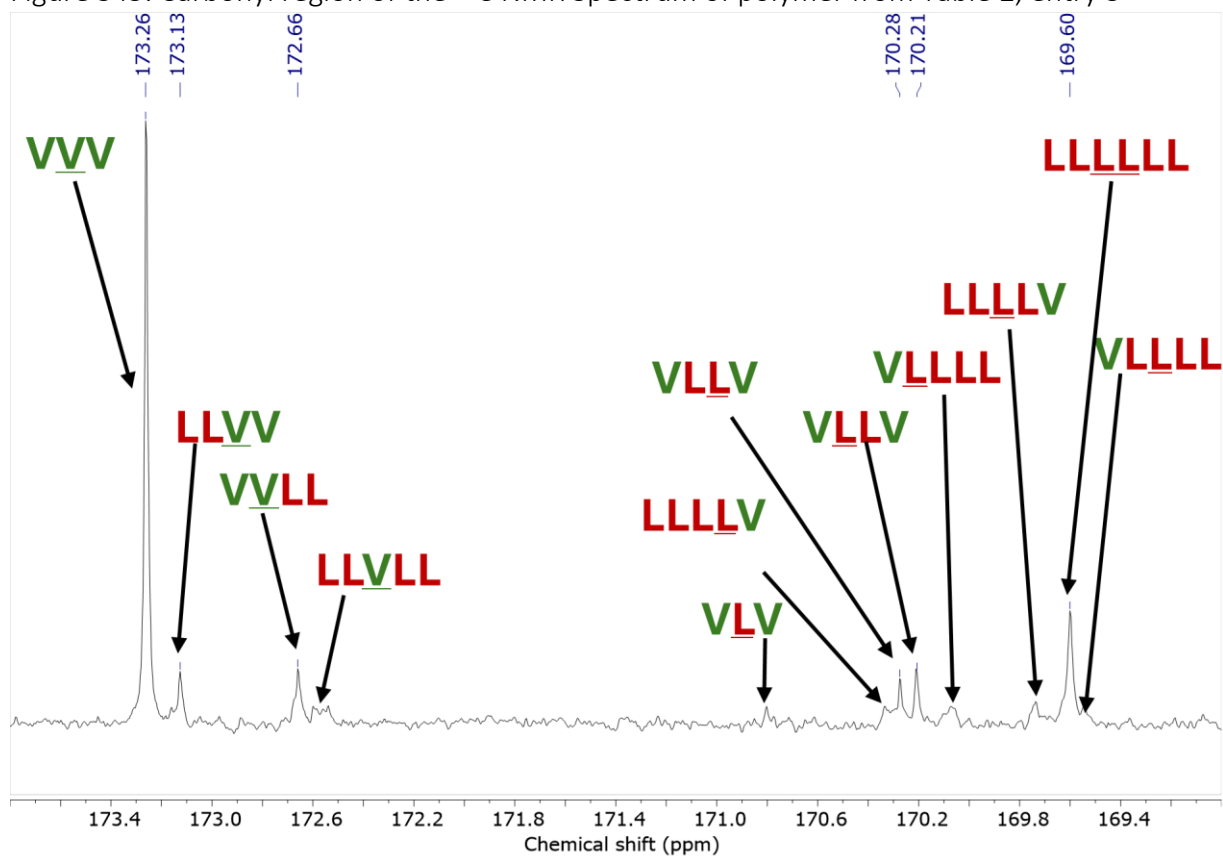
A very large, sharp peak is observed at 169.60 ppm, labeled **LLLLLL**, which corresponds to the carbonyl carbon of the repeating unit.

173.36
173.23
172.76
172.64
170.37
170.31
170.17
169.84
169.70

VVV
LLVV
VVLL
LLVLL
VLLV
LLLLV
VLLL
VLLL
LLLLV
VLLL
LLLLL

Chemical shift (ppm)

Figure S45: Carbonyl region of the ^{13}C NMR Spectrum of polymer from Table 2, entry 5



2. Representative GPC Traces of Copolymers

Figure S46: GPC Trace of sample from Table 1 entry 1

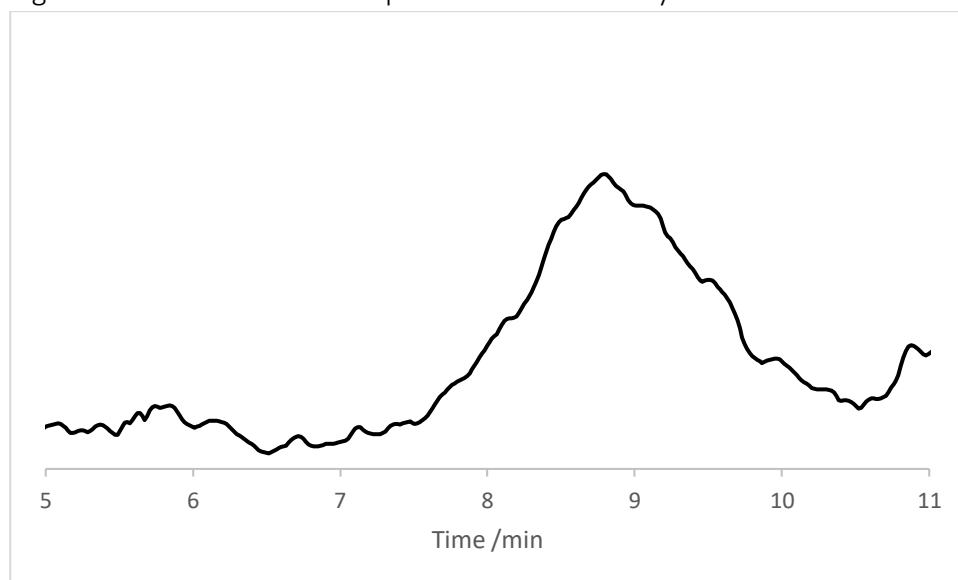


Figure S47: GPC Trace of sample from Table 1 entry 2

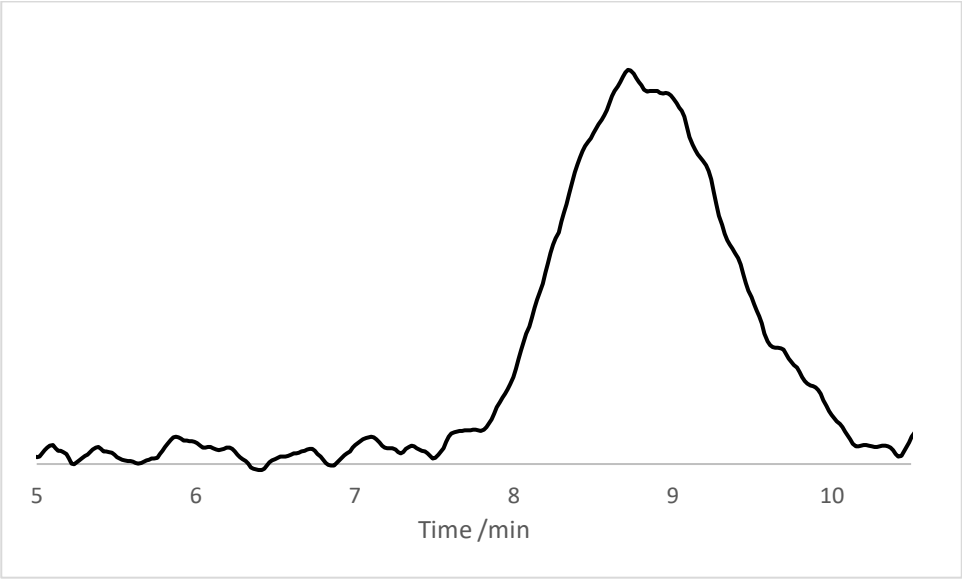


Figure S48: GPC Trace of sample from Table 1 entry 3

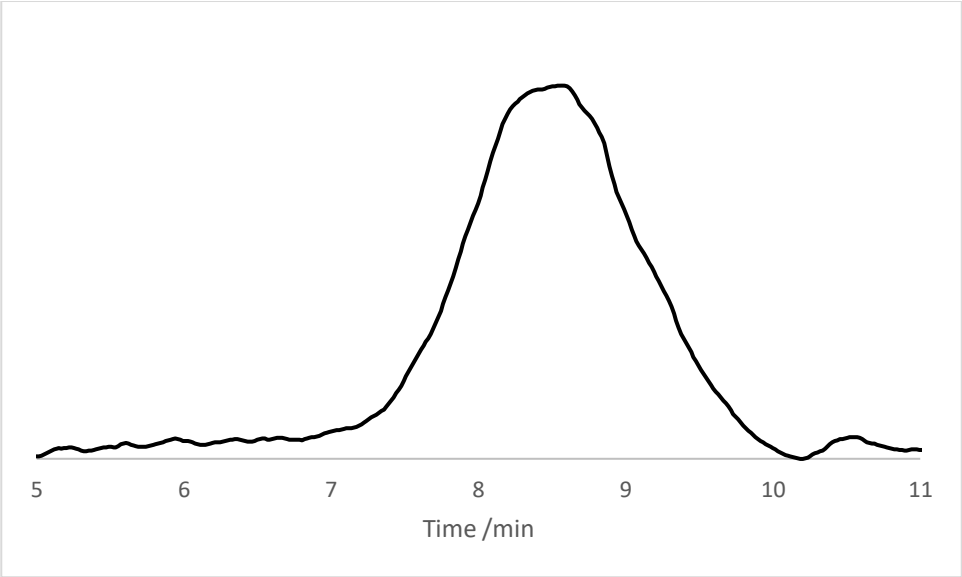


Figure S49: GPC Trace of sample from Table 1 entry 4

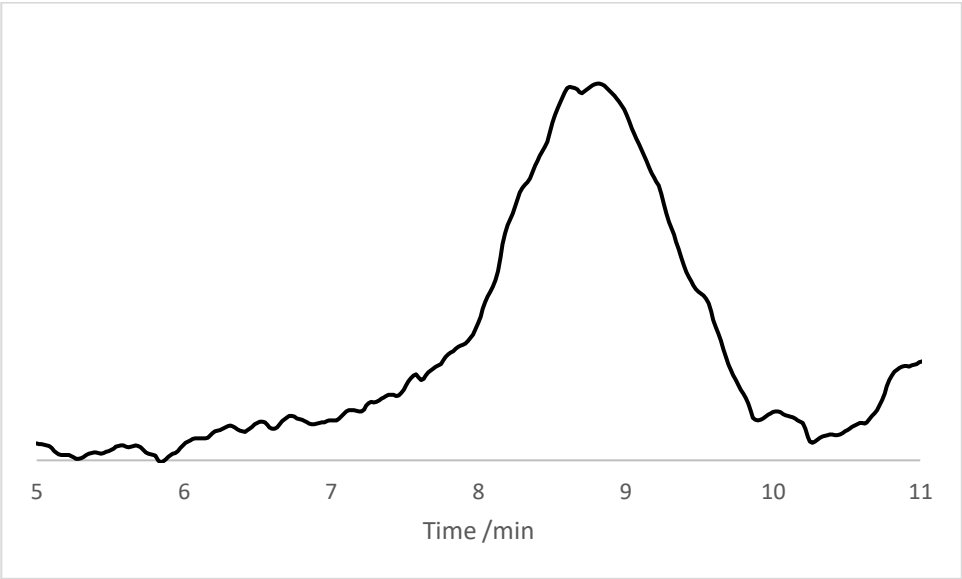


Figure S50: GPC Trace of sample from Table 1 entry 5

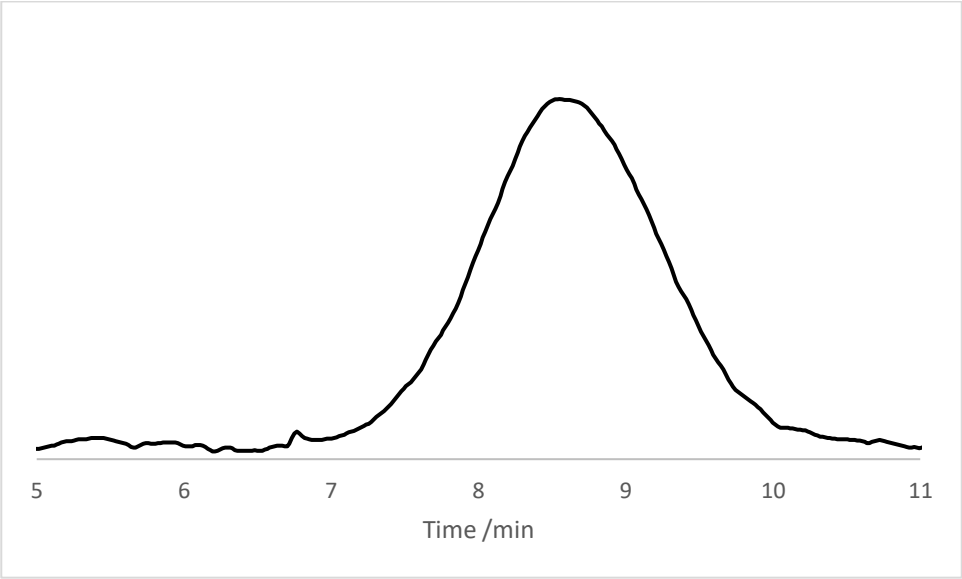


Figure S51: GPC Trace of sample from Table 1 entry 6

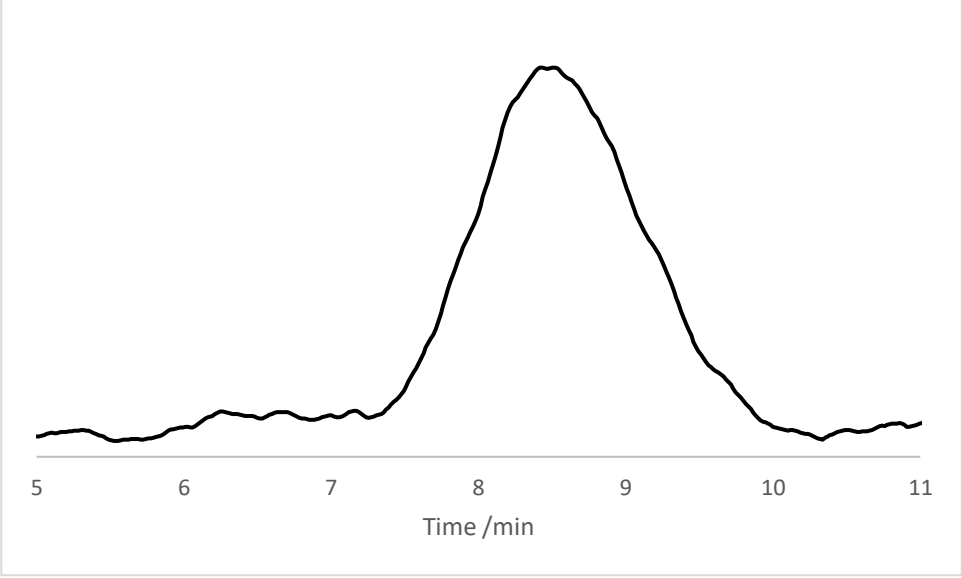


Figure S52: GPC Trace of sample from Table 1 entry 7

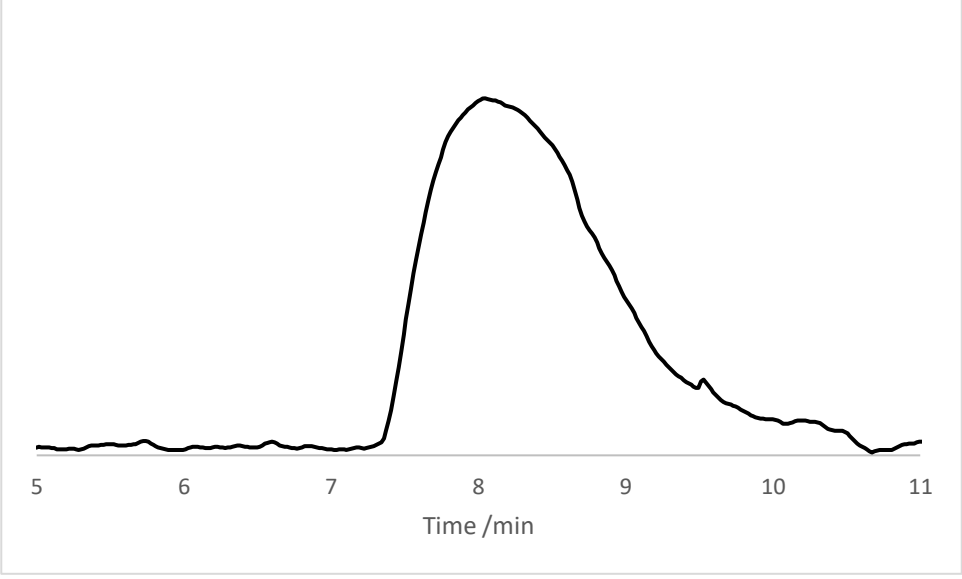


Figure S53: GPC Trace of sample from Table 1 entry 8

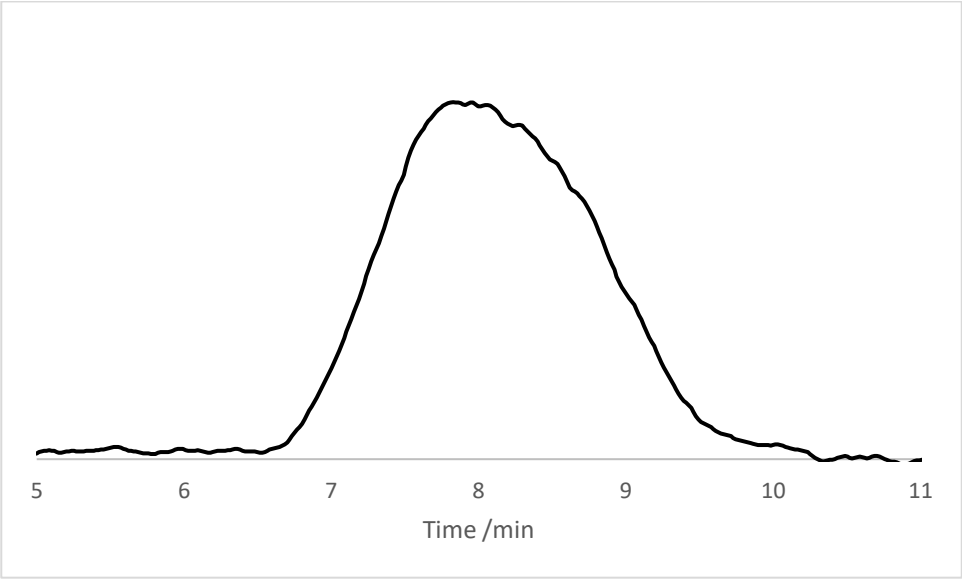


Figure S54: GPC Trace of sample from Table 1 entry 9

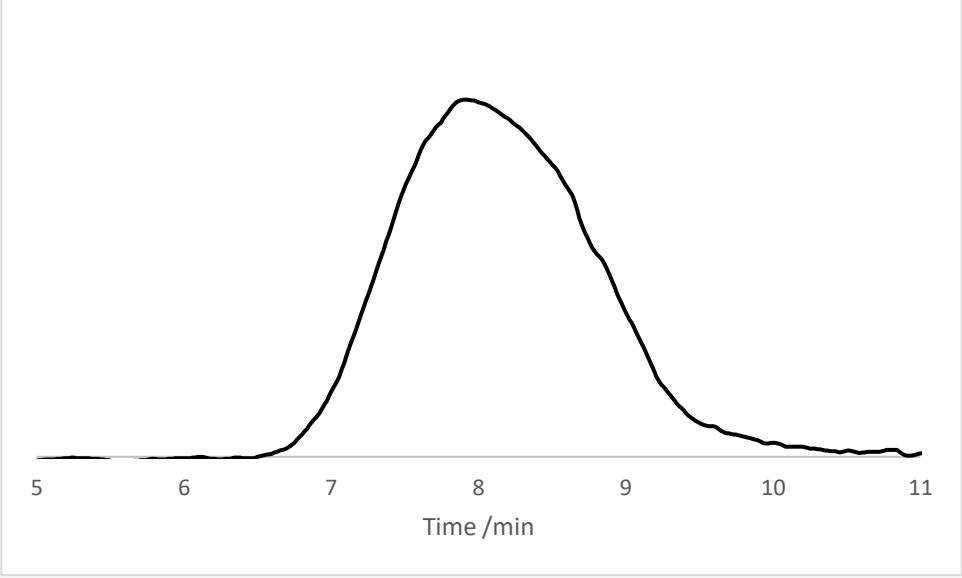


Figure S55: GPC Trace of sample from Table 1 entry 10

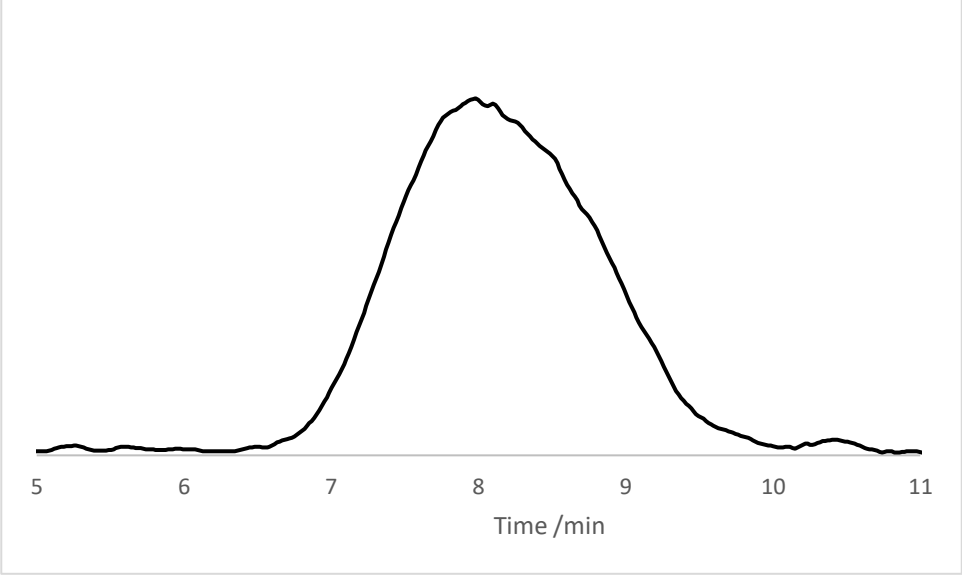


Figure S56: GPC Trace of sample from Table 1 entry 11

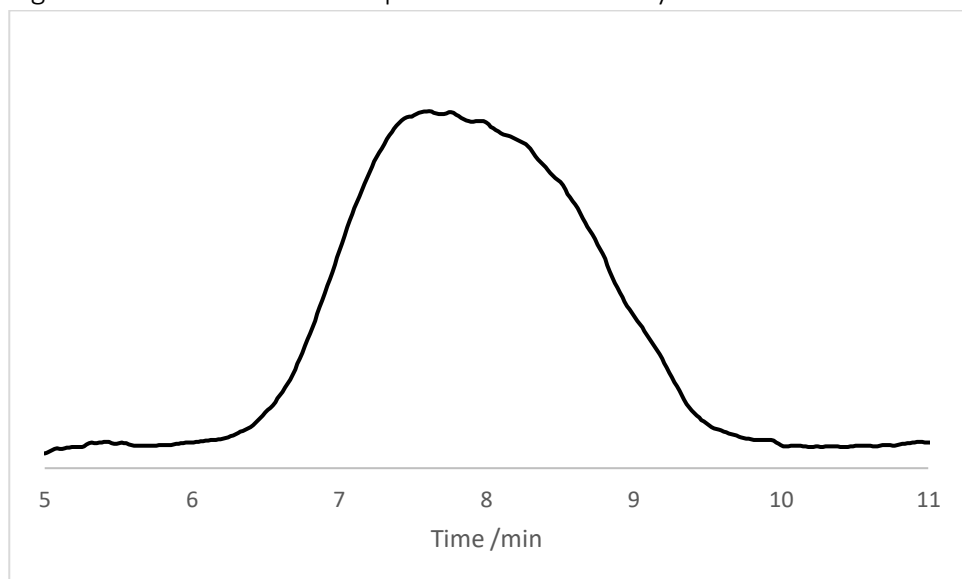
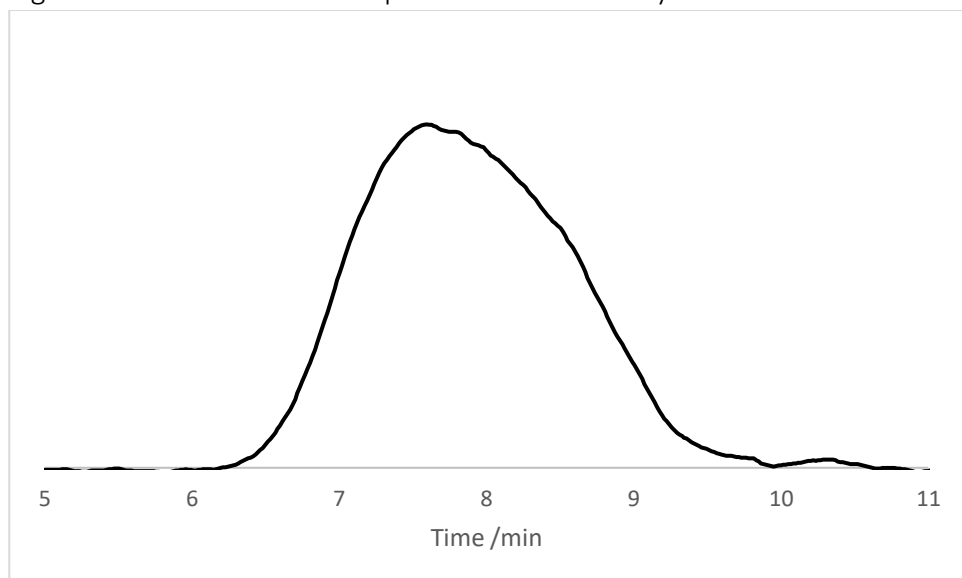
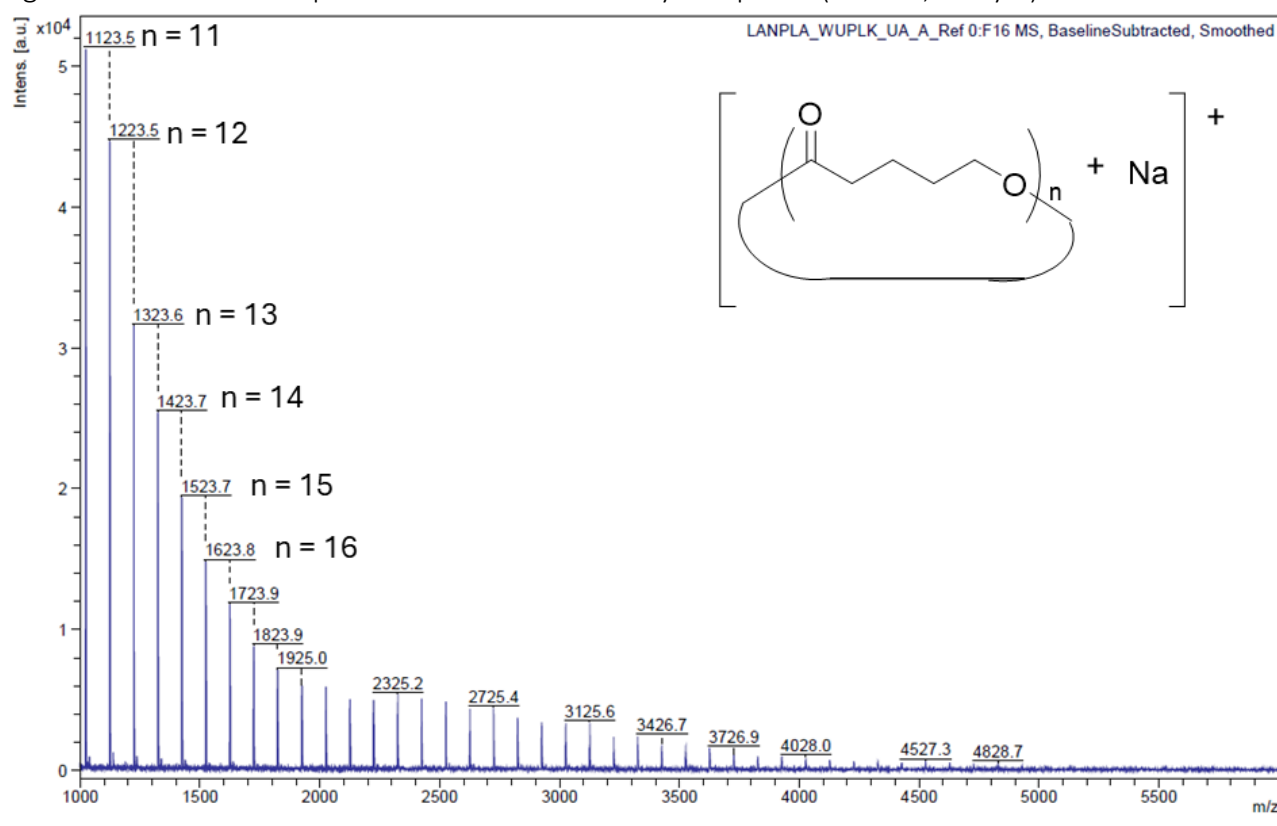


Figure S57: GPC Trace of sample from Table 1 entry 12



3. MALDI-ToF Data

Figure S58: MALDI-ToF spectrum of a PVL formed by complex **3** (Table 1, entry 7).



4. DOSY NMR Spectra of Copolymers

Figure S59: ^1H DOSY NMR spectrum of a copolymer prepared by complex **1**.

*Reaction conditions: $[\text{rac-LA}]_0 = [\delta\text{-VL}]_0 = 0.5 \text{ M}$ in toluene, $[\text{rac-LA}]_0/[\mathbf{1}] = 10$, reaction time: 20 min.

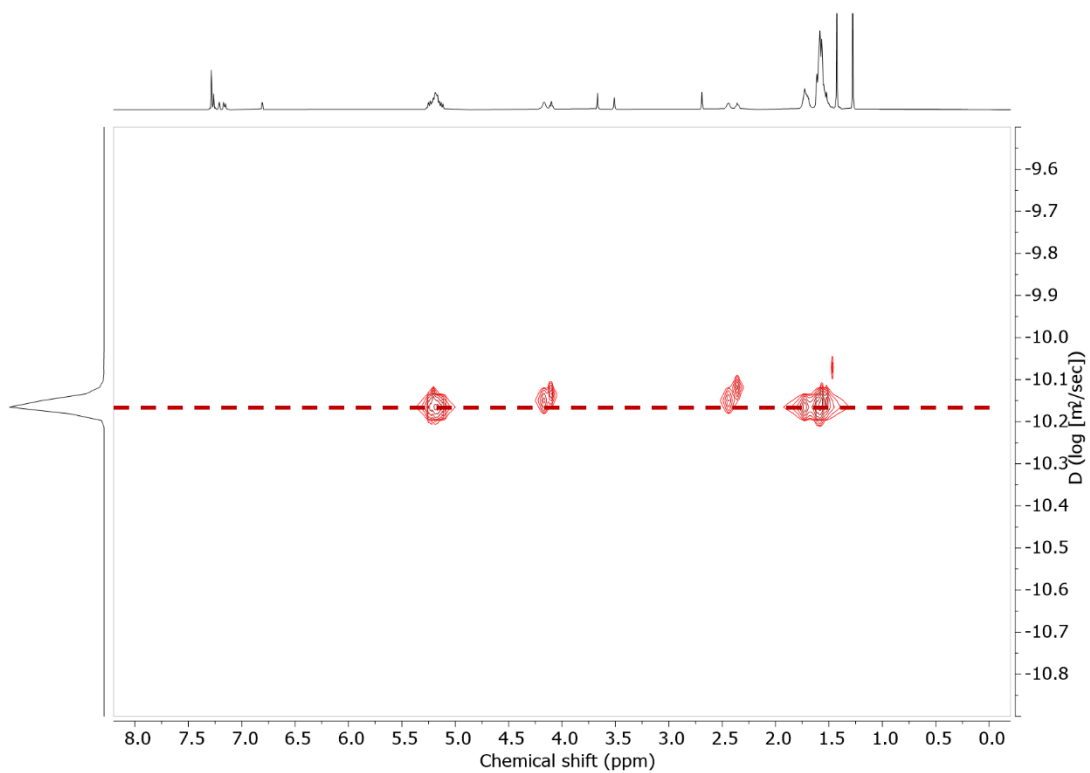
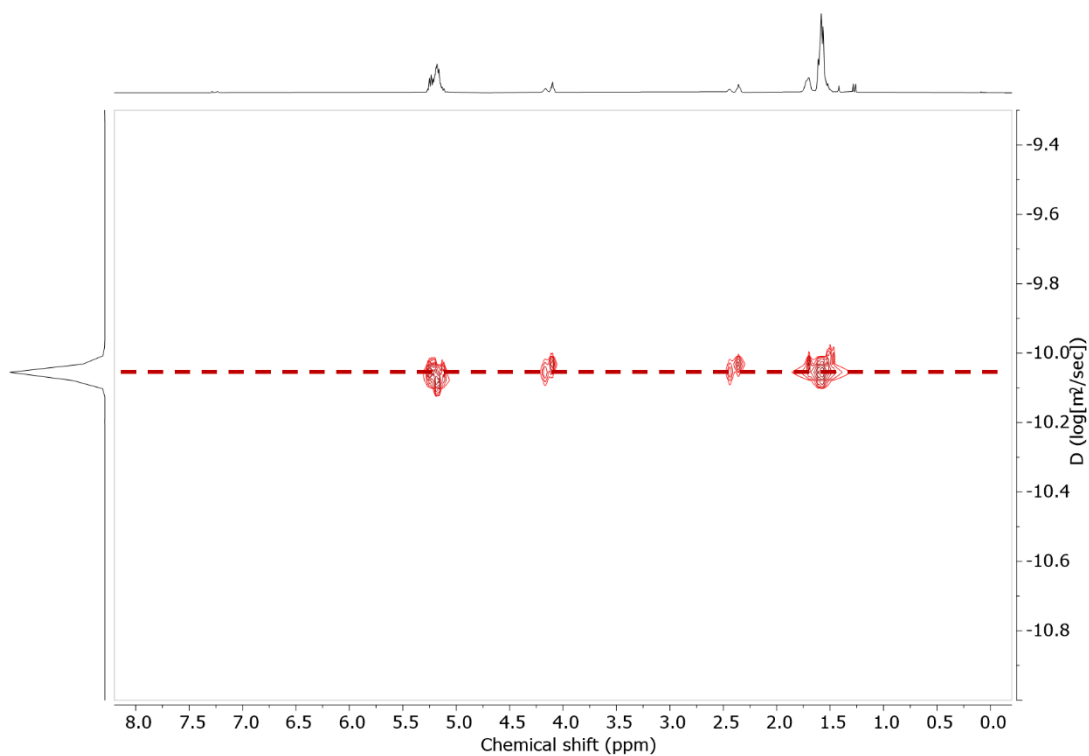


Figure S60: ^1H DOSY NMR spectrum of a copolymer prepared by complex **2**.

*Reaction conditions: $[\text{rac-LA}]_0 = [\delta\text{-VL}]_0 = 0.5\text{ M}$ in toluene, $[\text{rac-LA}]_0/[\mathbf{2}] = 10$, reaction time: 20 min.



4. DSC Traces of Copolymers

In each case, the first cooling cycle and second heating cycle are displayed.

Figure S61: DSC trace for Table 4, Entry 1

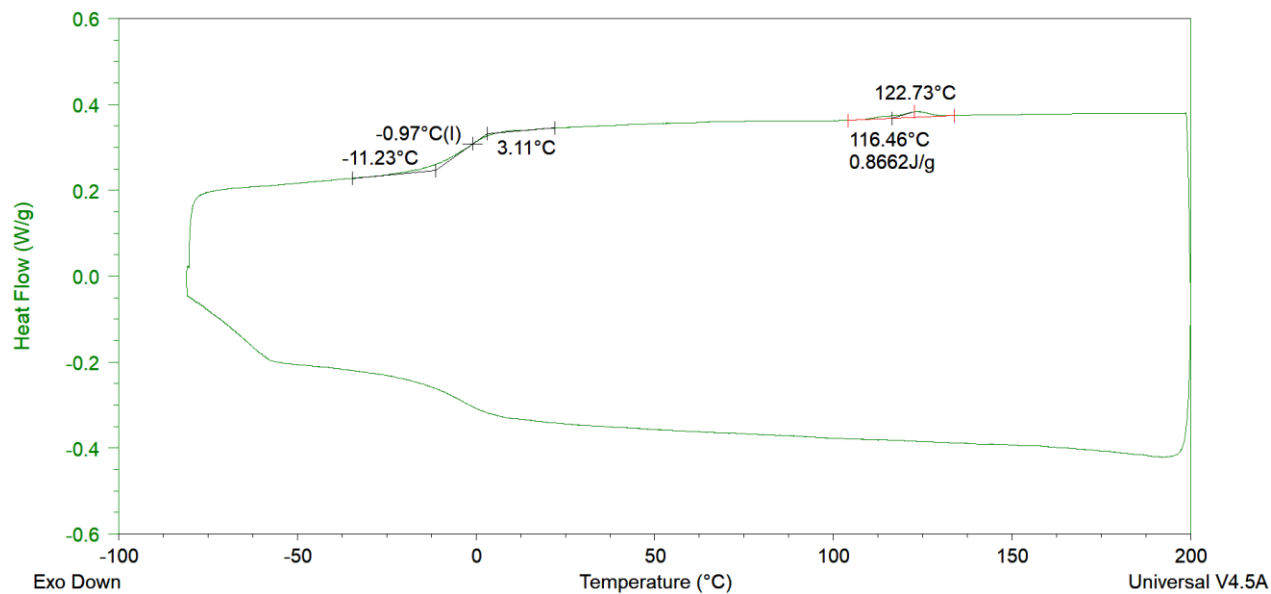


Figure S62: DSC trace for Table 4, Entry 2

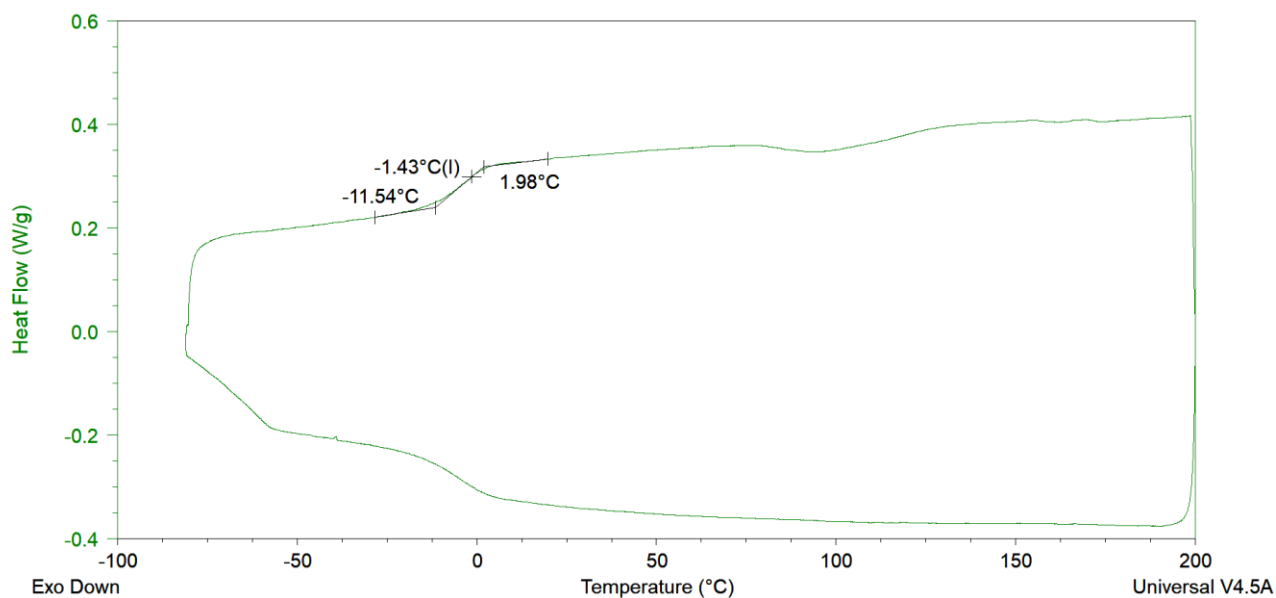


Figure S63: DSC trace for Table 4, Entry 3

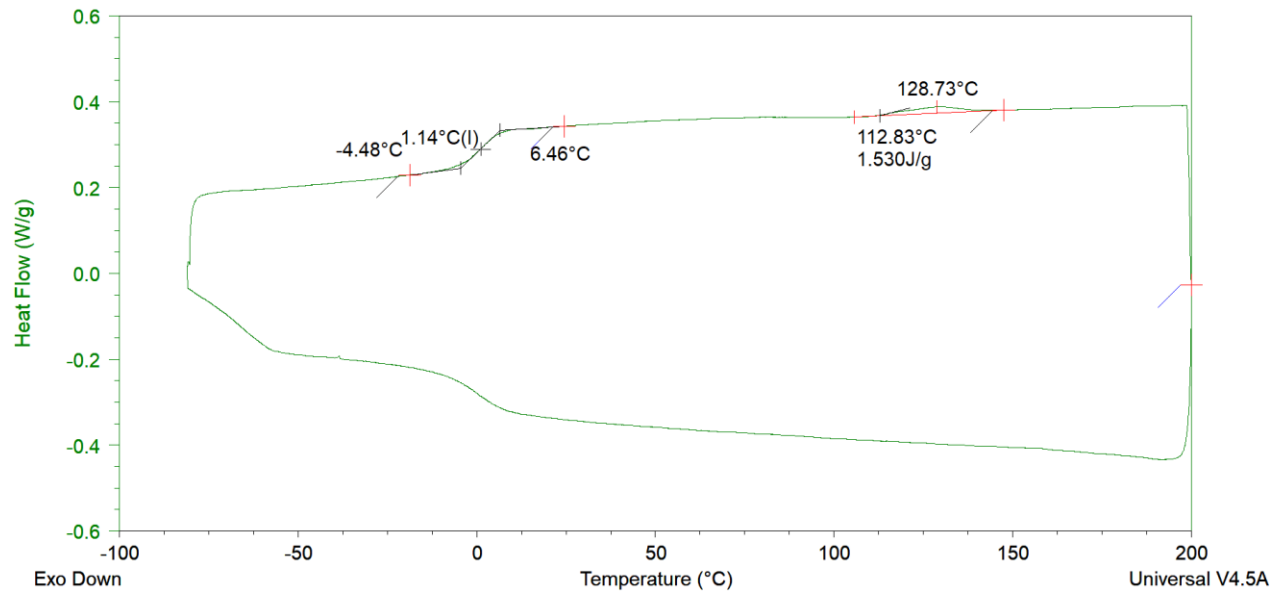


Figure S64: DSC trace for Table 4, Entry 4

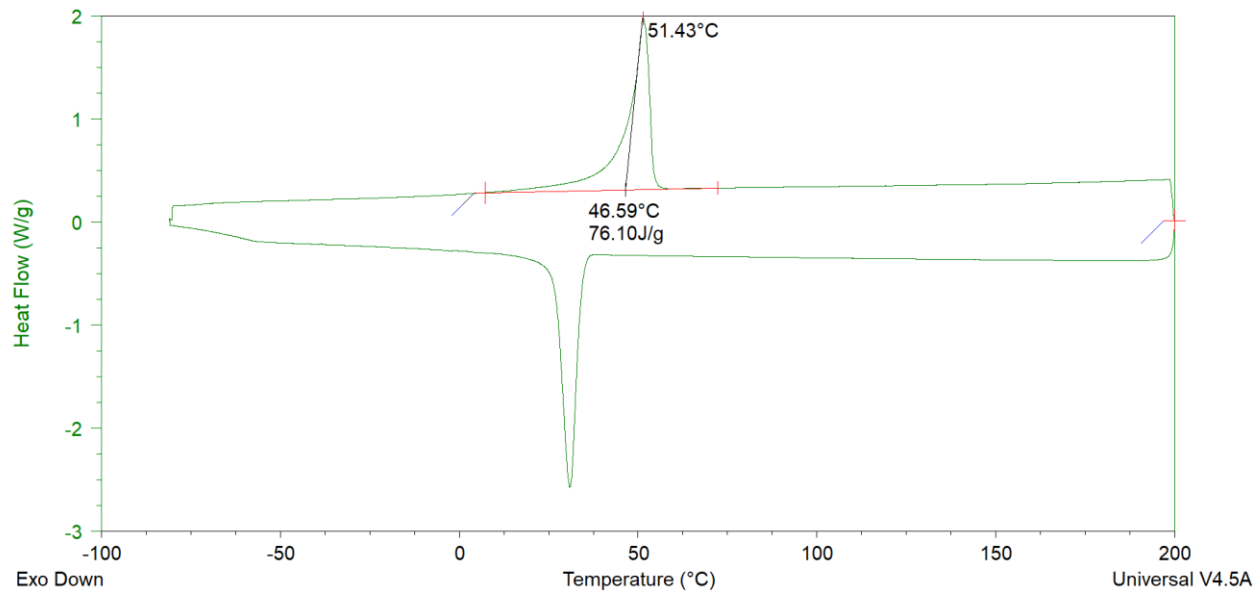


Figure S65: DSC trace for Table 4, Entry 5

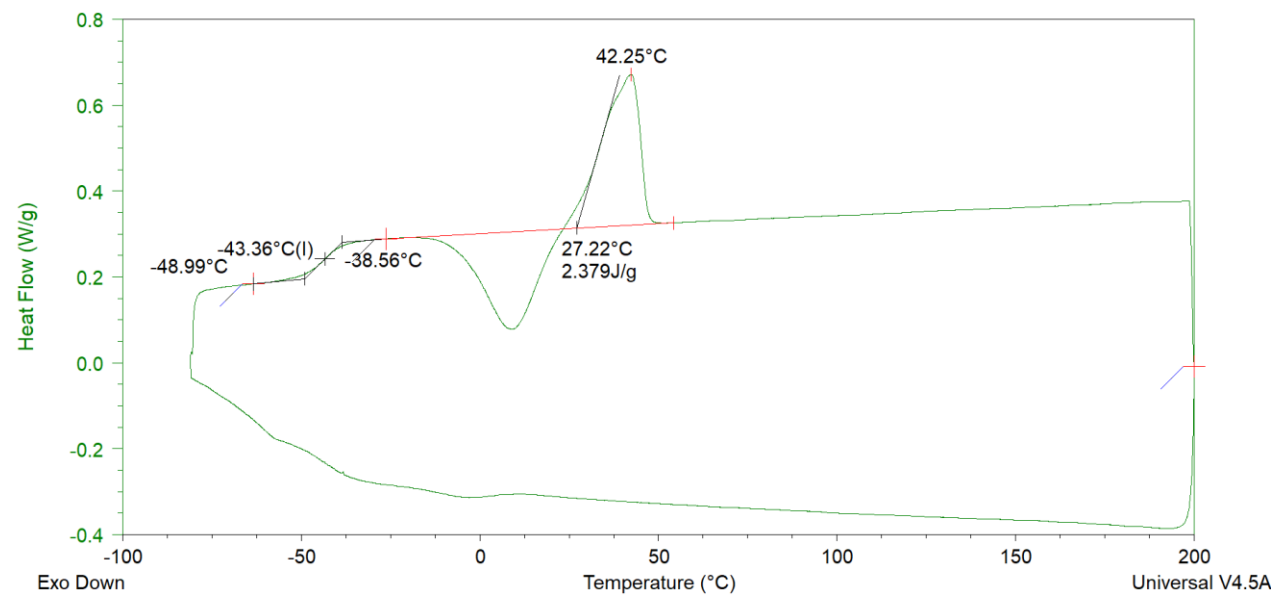


Figure S66: DSC trace for Table 4, Entry 6

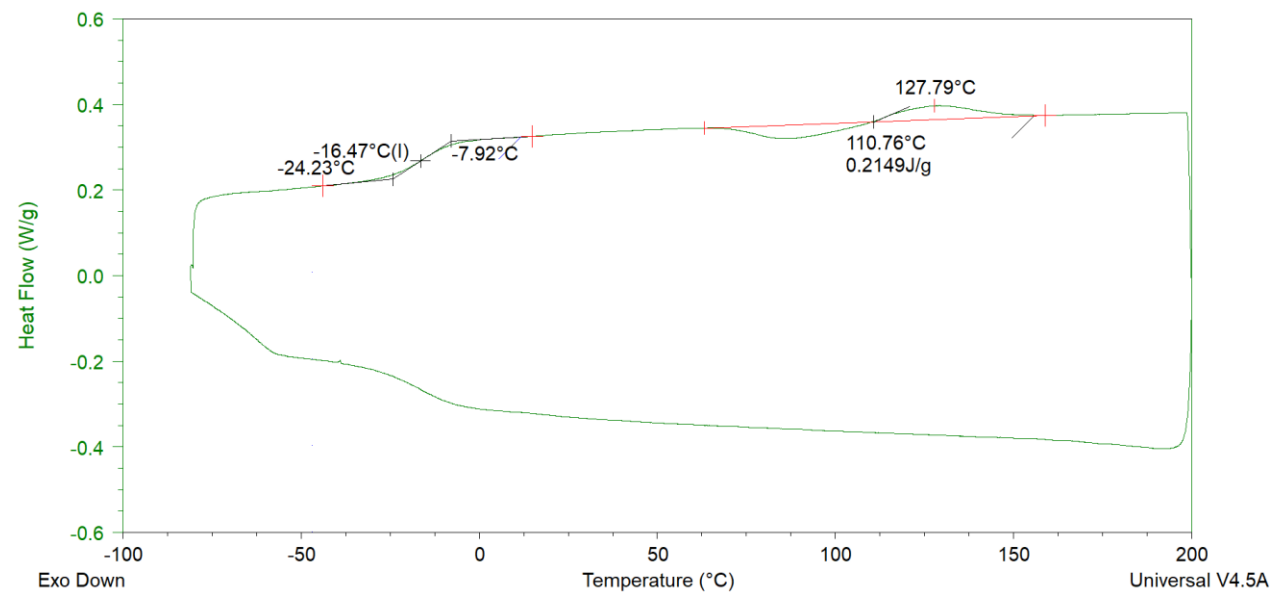


Figure S67: DSC trace for Table 4, Entry 7

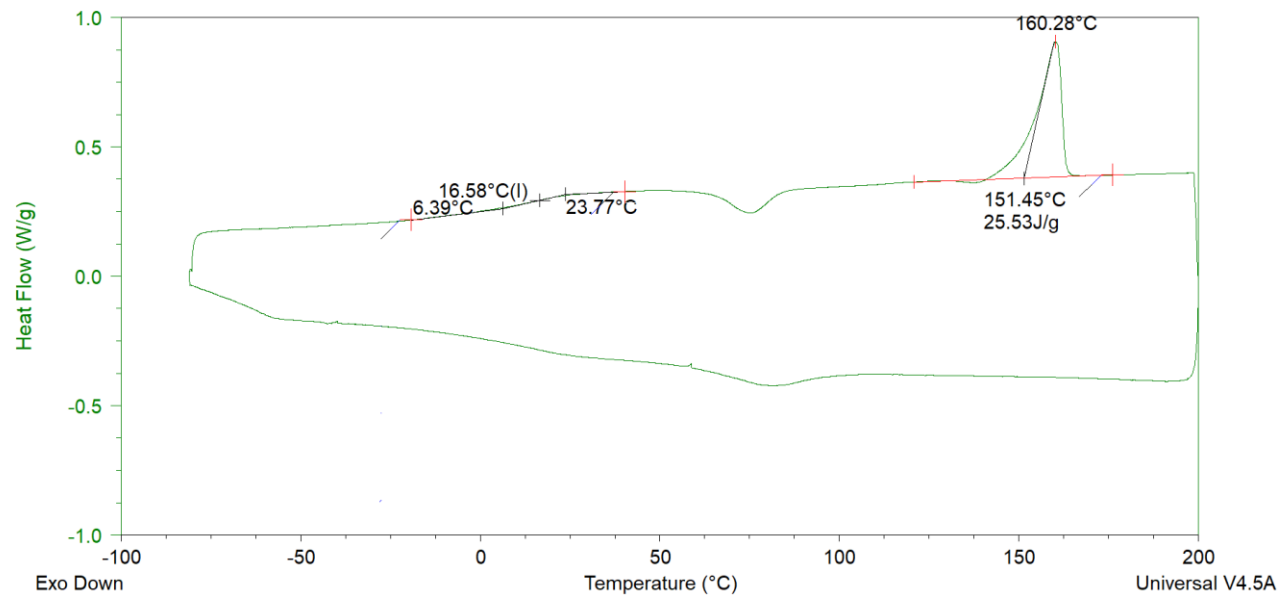


Figure S68: DSC trace for Table 4, Entry 8

