SUPPLEMENTARY INFORMATION FOR:

Terpolymers derived from Limonene Oxide and Carbon Dioxide: Access to Cross-Linked Polycarbonates with Improved Thermal Properties

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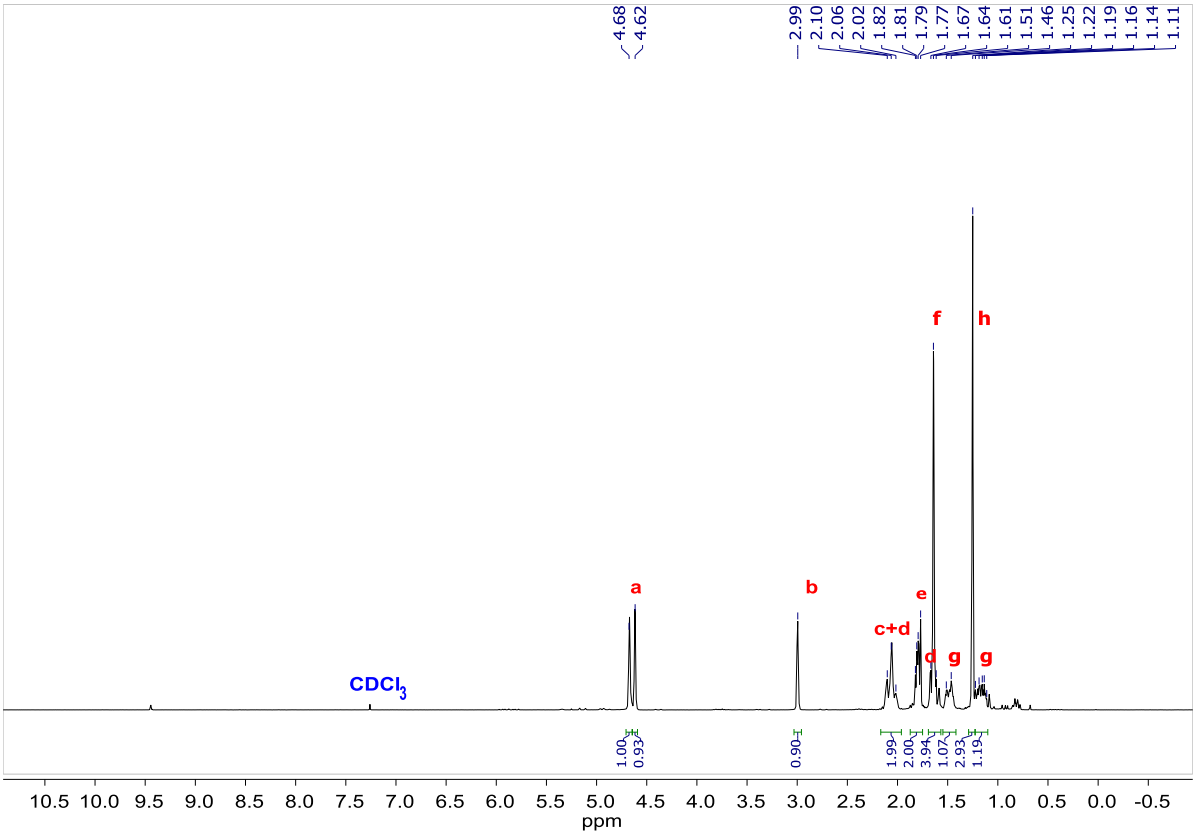
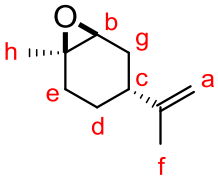
NMR SPECTRA:[1]

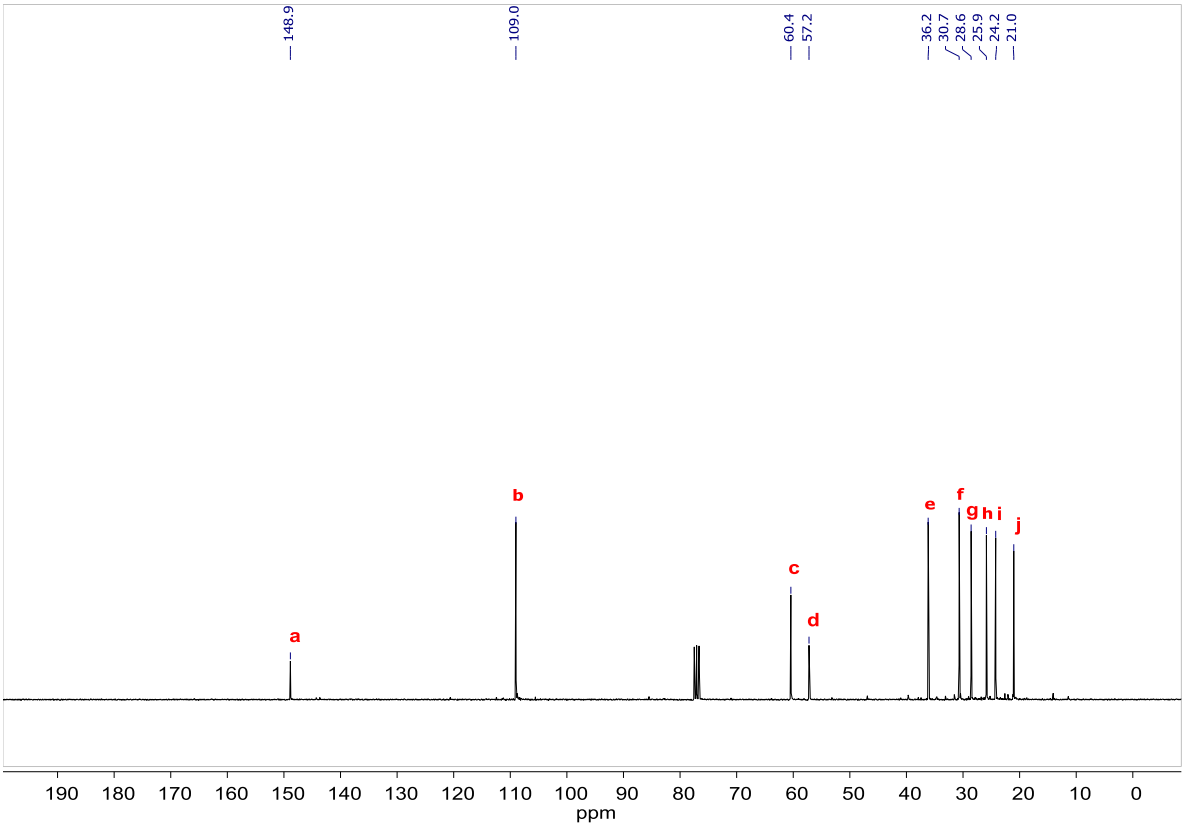
Figure S1. ^{1}H NMR spectrum of *cis*-(*R*)-limonene oxide in $CDCl_3$ (400 MHz) at RT.

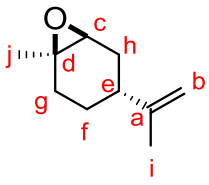




^{1}H NMR ($CDCl_3$, 400 MHz, RT): δ = 4.68 (s, 1H), 4.62 (s, 1H), 2.99 (s, 1H), 2.13-2.00 (m, 2H), 1.83-1.75 (m, 2H), 1.68-1.58 (m, 1H), 1.64 (s, 3H), 1.54-1.43 (m, 1H), 1.25 (s, 3H), 1.23-1.08 (m, 1H).

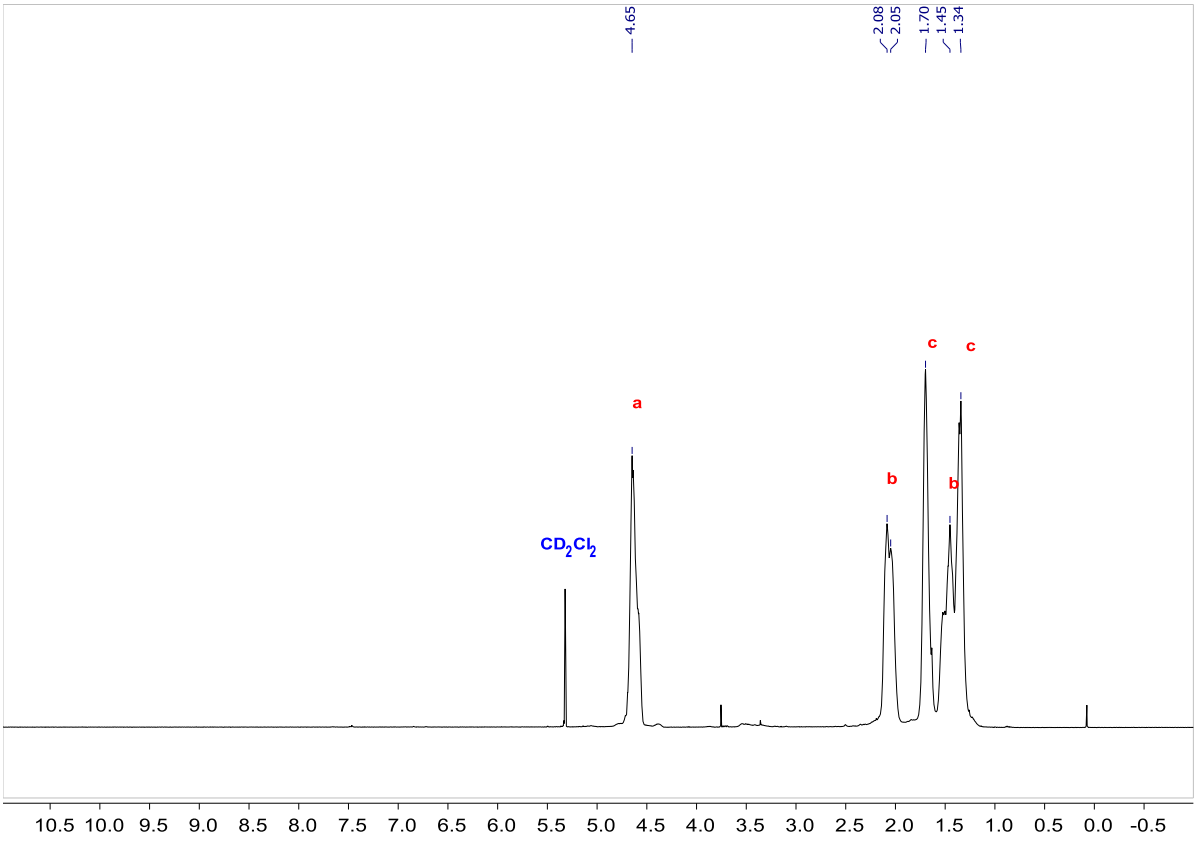
Figure S2. ^{13}C NMR spectrum of *cis*-(*R*)-limonene oxide in $CDCl_3$ (101 MHz) at RT.

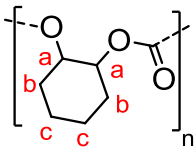




$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz, RT): δ = 148.9 (C_q, C=CH_2), 109.0 (C=CH$_2$), 60.4 (OCH), 57.2 (OC_q), 36.2 (CH), 30.7 (CH$_2$), 28.6 (CH$_2$), 25.9 (CH$_2$), 24.2 (CH$_3$), 21.0 (CH$_3$).

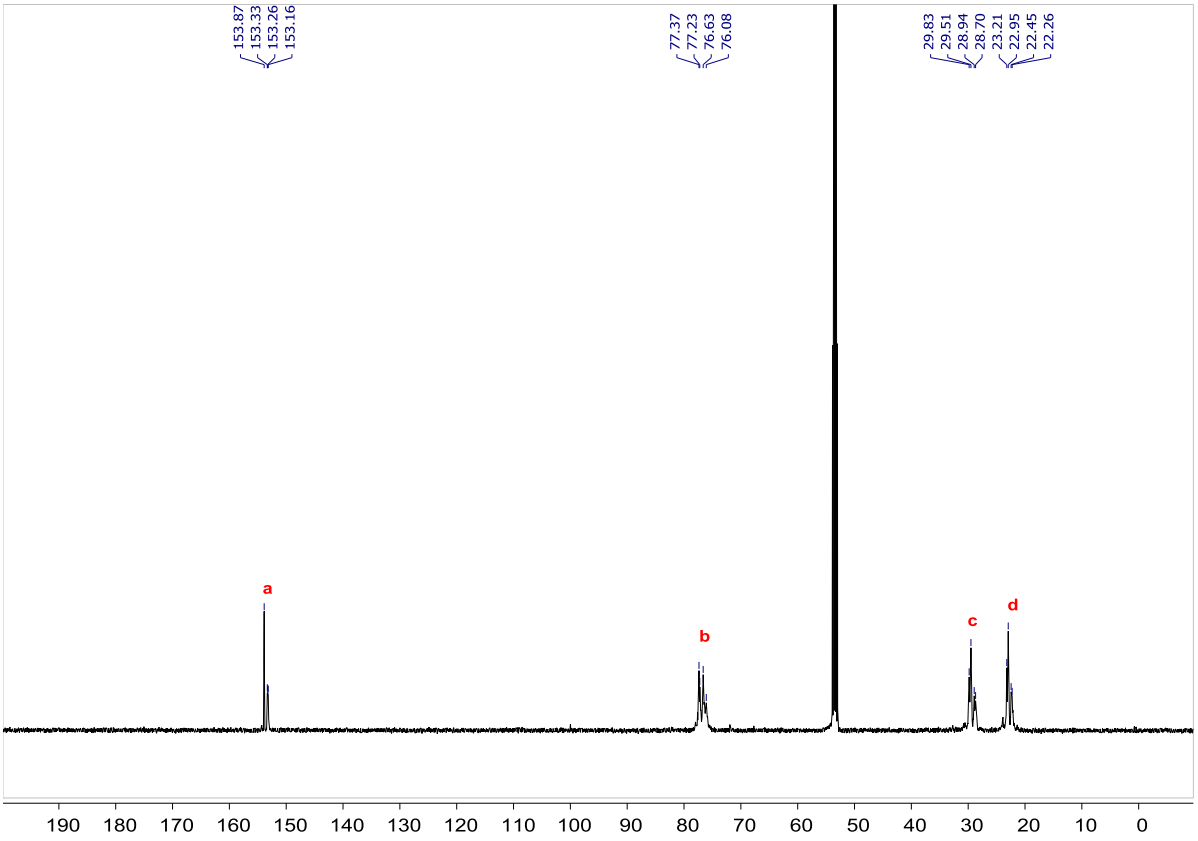
Figure S3. ^{1}H NMR spectrum of CHO/CO_2 copolymer (**P-0**) in CD_2Cl_2 (400 MHz) at RT.

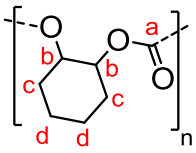




^{1}H NMR (CD_2Cl_2, 400 MHz, RT): δ = 4.65 (m br, 2H), 2.15-1.97 (m br, 2H), 1.78-1.61 (m br, 2H), 1.57-1.41 (m br, 2H), 1.40-1.26 (m br, 2H).

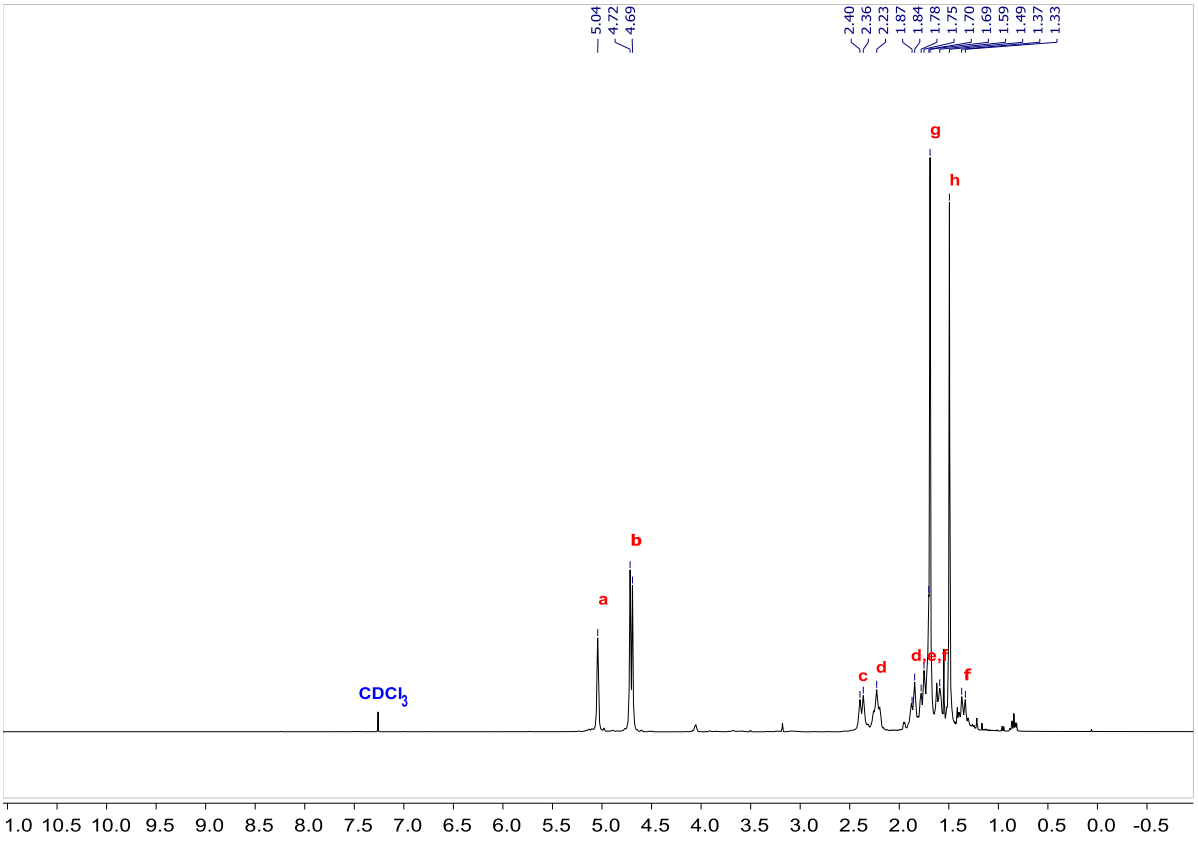
Figure S4. ^{13}C NMR spectrum of CHO/CO_2 copolymer (**P-0**) in CD_2Cl_2 (101 MHz) at RT.

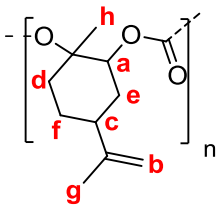




$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 101 MHz, RT): δ = 153.9 (C_q, *C*=O), 153.3-153.1 (C_q, *C*=O), 77.4-76.0 (O*C*H), 29.8-28.7 (*C*H_2), 23.2-22.3 (*C*H_2).

Figure S5. ^{1}H NMR spectrum of LO/CO_2 copolymer (**P-100**) in $CDCl_3$ (400 MHz) at RT.

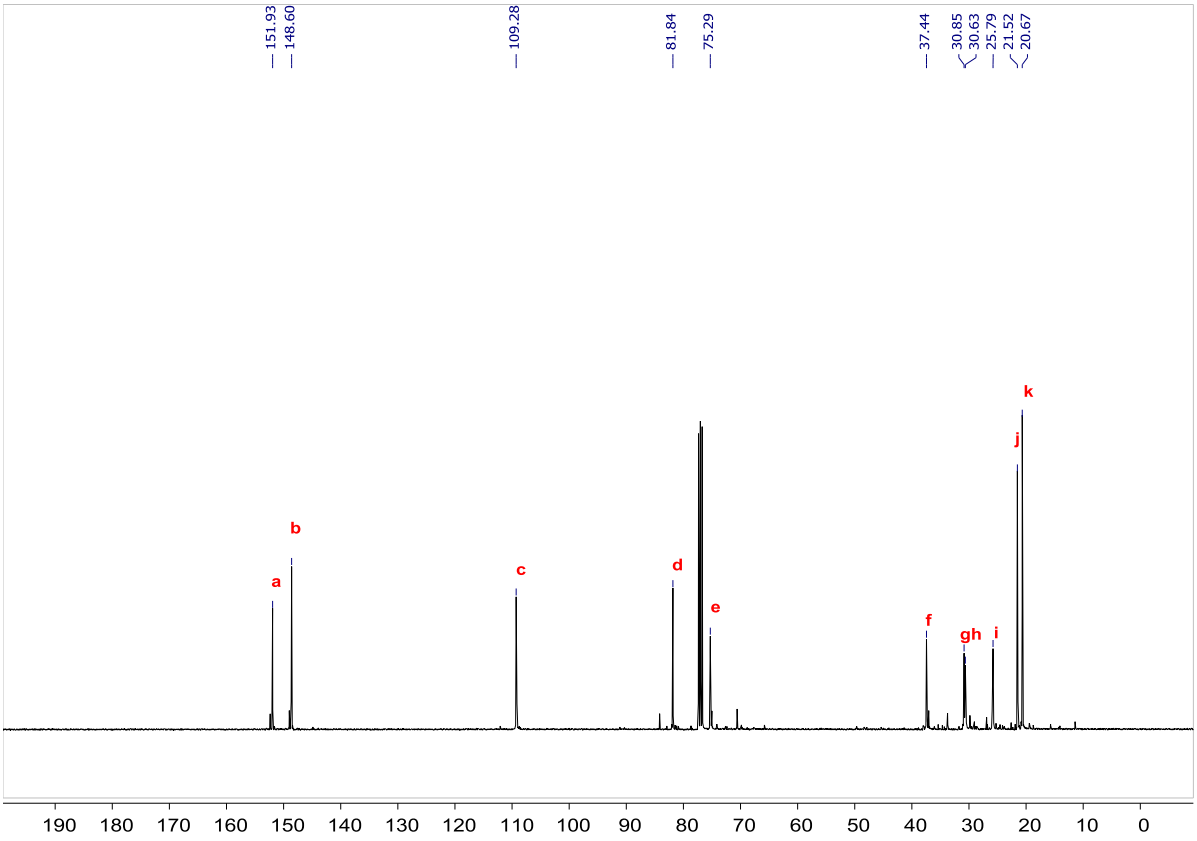


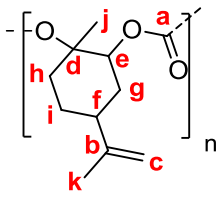


^{1}H NMR ($CDCl_3$, 400 MHz, RT): δ = 5.04 (s br, 1H), 4.72 (s, 1H), 4.69 (s, 1H), 2.39 (m br, 1H), 2.24 (m br, 1H), 1.90-1.56 (m br, 4H), 1.70 (s, 3H), 1.50 (s, 3H), 1.43-1.30 (m br, 1H).

*LO terminal group: 4.60 and 4.65 ppm

Figure S6. ^{13}C NMR spectrum of LO/CO_2 copolymer (**P-100**) in $CDCl_3$ (101 MHz) at RT.

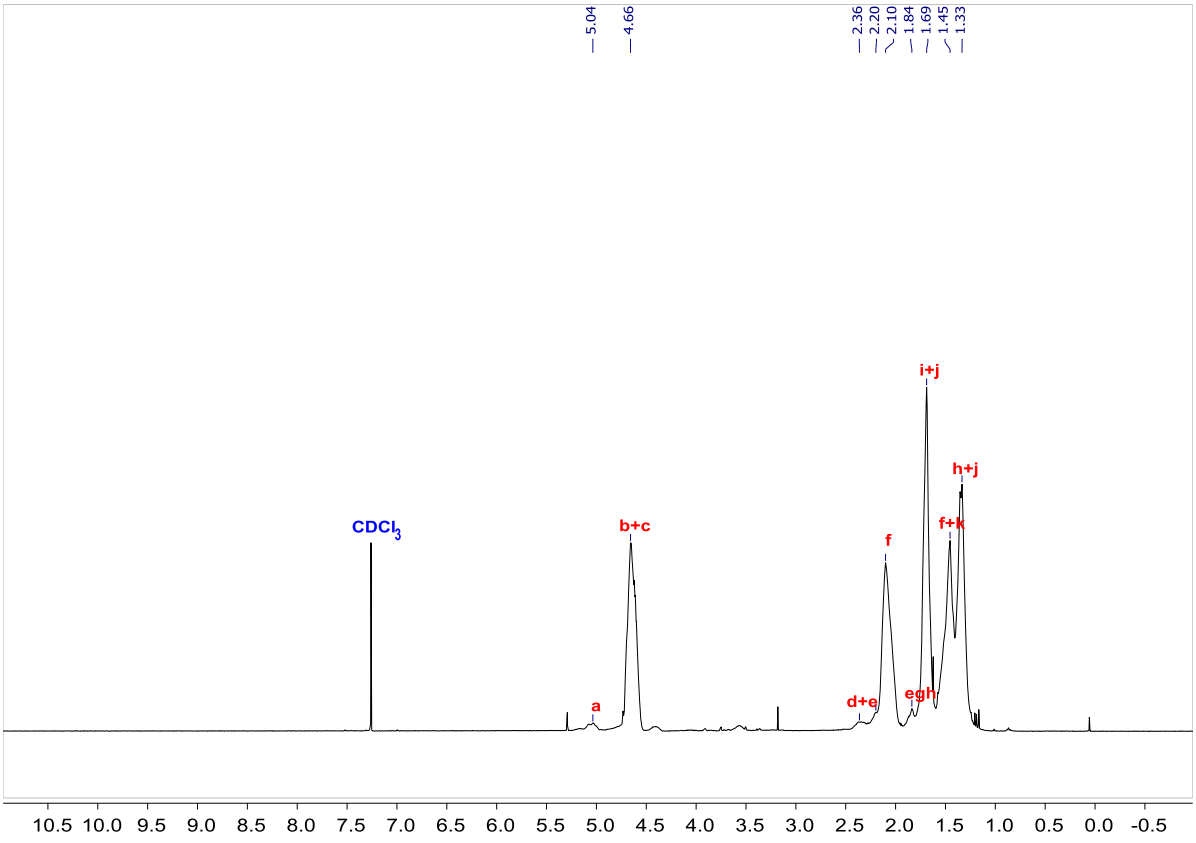


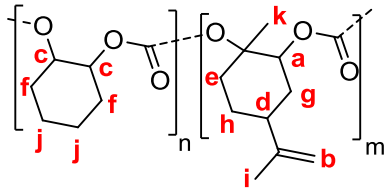


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 MHz, RT): δ = 152.0 (C_q, *C*=O), 148.6 (C_q, *C*=CH_2), 109.3 (C=*C*H_2), 81.8 (C_q, O*C*), 75.3 (O*C*H), 37.4 (*C*H), 30.9 (*C*H_2), 30.6 (*C*H_2), 25.8 (*C*H_2), 21.5 (*C*H_3), 20.7 (*C*H_3).

*LO terminal group: 70.6 and 77.2 ppm

Figure S7. ^{1}H NMR spectrum of terpolymer **T-10** in $CDCl_3$ (400 MHz) at RT.

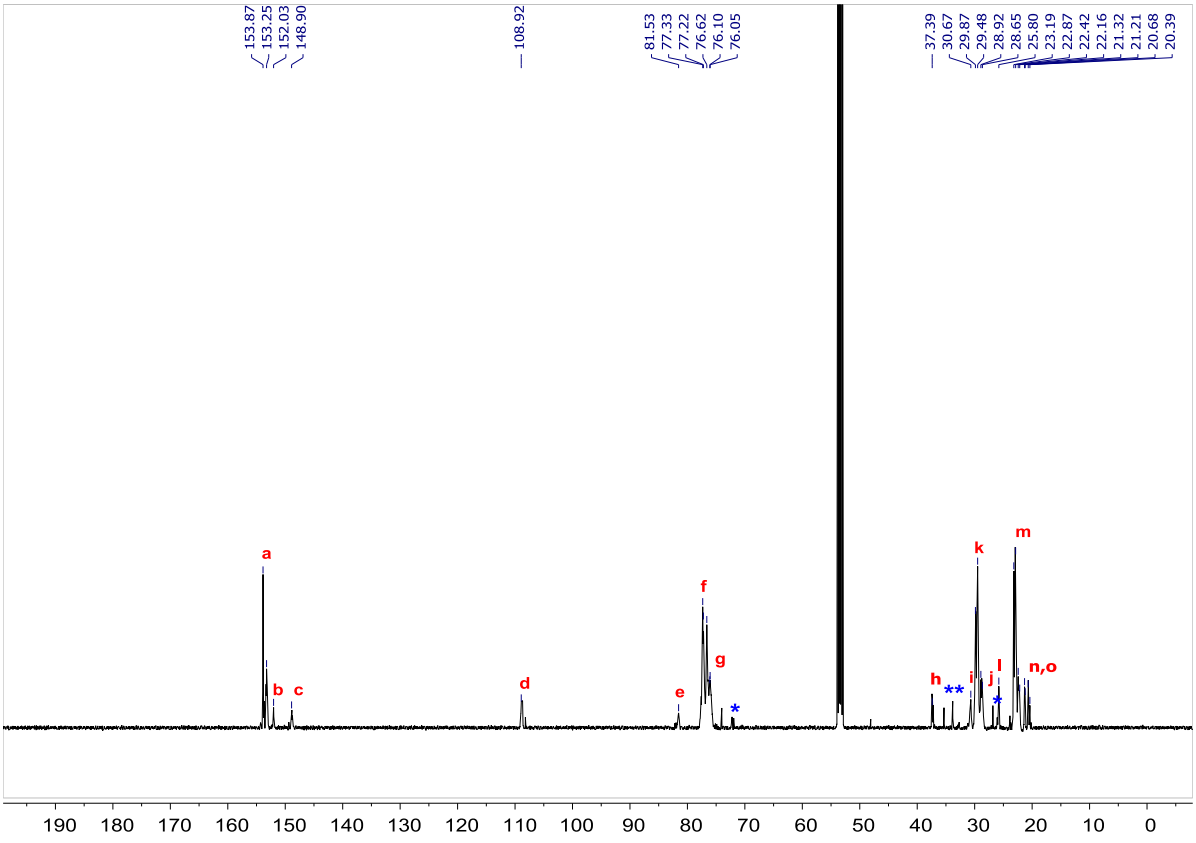


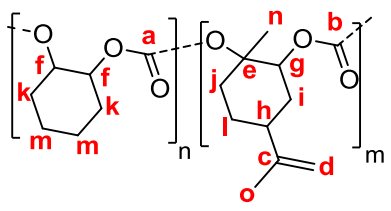


^{1}H NMR ($CDCl_3$, 400 MHz, RT): δ = 5.04 (s br, 1H^{LO}), 4.75-4.57 (m br, 2H^{CHO} + 2H^{LO}), 2.43-2.30 (m br, 1H^{LO}), 2.25-2.17 (m br, 1H^{LO}), 2.11 (m br, 2H^{CHO}), 1.90-1.56 (m br, 4H^{LO}), 1.69 (m br, 2H^{CHO} + 3H^{LO}), 1.58-1.45 (m br, 2H^{CHO} + 3H^{LO}), 1.42-1.23 (m br, 2H^{CHO} + 1H^{LO}).

*CHO terminal group: 4.40 and 3.58 ppm

Figure S8. ^{13}C NMR spectrum of terpolymer **T-10** in CD_2Cl_2 (101 MHz) at RT.



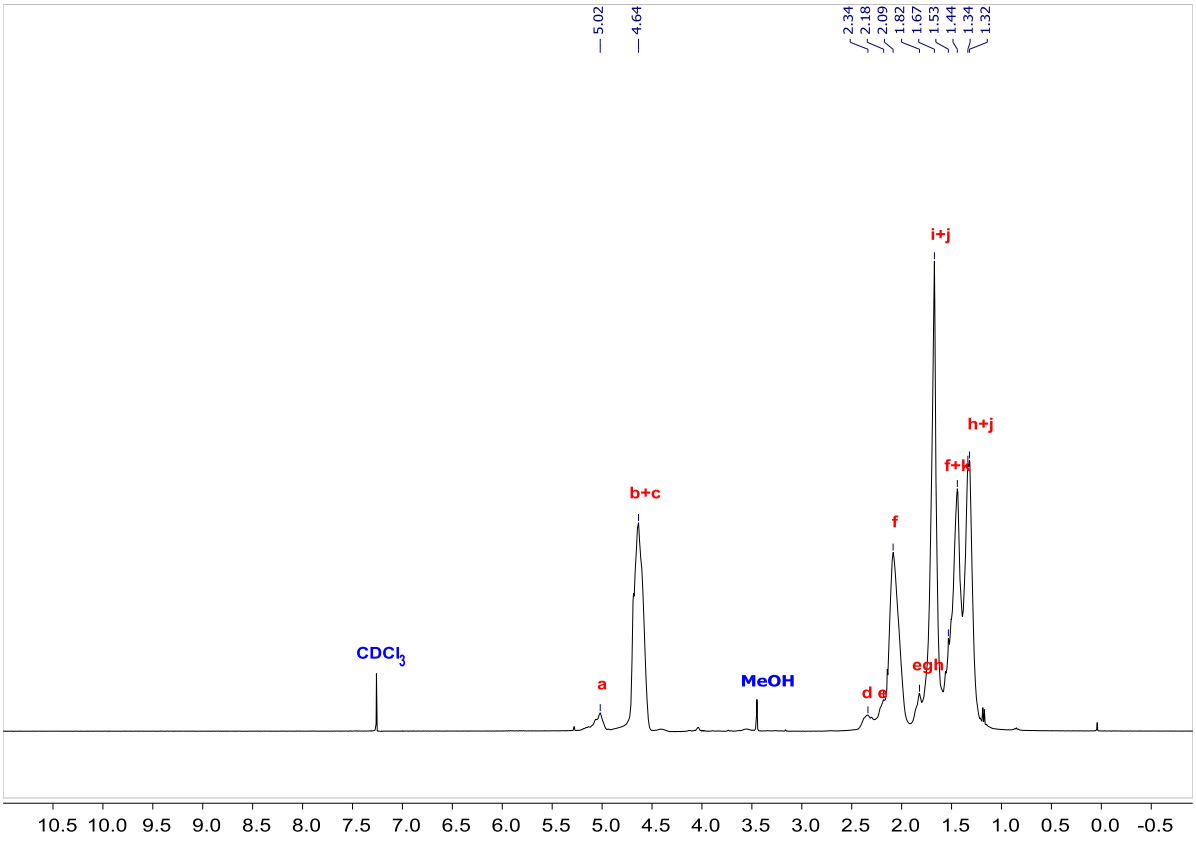


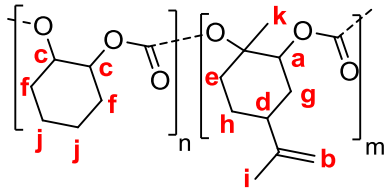
$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 400 MHz, RT): δ = 153.9 (C_q, C=O^{CHO}), 153.3-153.2 (C_q, C=O^{CHO}), 152.1-151.9 (C_q, C=O^{LO}), 149.9-148.7 (C_q, C=CH$_2^{LO}$), 108.9 (C=CH$_2^{LO}$), 81.5 (C_q, OC^{LO}), 77.3-76.6 (OCH^{CHO}), 76.1 (OCH^{LO}), 37.5-37.2 (CH^{LO}), 30.9-30.5 (CH$_2^{LO}$), 29.8-29.1 (CH$_2^{CHO}$), 29.0-28.5 (CH$_2^{LO}$), 25.8 (CH$_2^{LO}$), 23.2-22.7 (CH$_2^{CHO}$), 22.5-22.1 (CH$_3^{LO}$), 21.3-20.6 (CH$_3^{LO}$).

*CHO terminal group: 72.1 ppm

*For the LO ether linkages: 71.9, 35.4, 33.8, 26.8 ppm

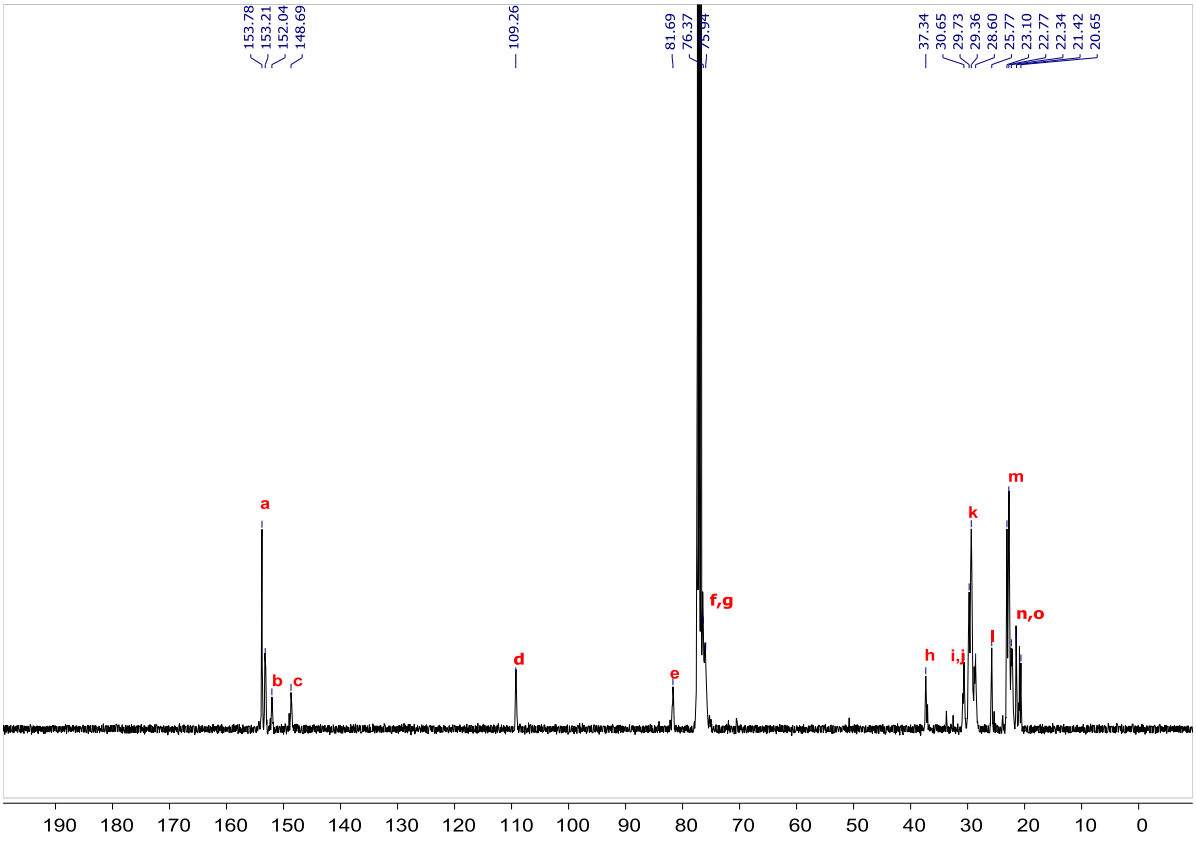
Figure S9. ^{1}H NMR spectrum of terpolymer **T-20** in $CDCl_3$ (400 MHz) at RT.

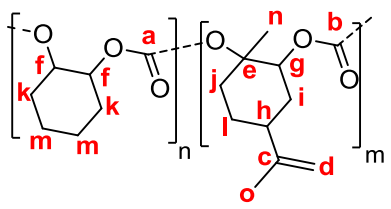




^{1}H NMR ($CDCl_3$, 400 MHz, RT): δ = 5.04 (s br, 1H^{LO}), 4.75-4.57 (m br, 2H^{CHO} + 2H^{LO}), 2.43-2.30 (m br, 1H^{LO}), 2.25-2.17 (m br, 1H^{LO}), 2.11 (m br, 2H^{CHO}), 1.90-1.56 (m br, 4H^{LO}), 1.69 (m br, 2H^{CHO} + 3H^{LO}), 1.58-1.45 (m br, 2H^{CHO} + 3H^{LO}), 1.42-1.23 (m br, 2H^{CHO} + 1H^{LO}).

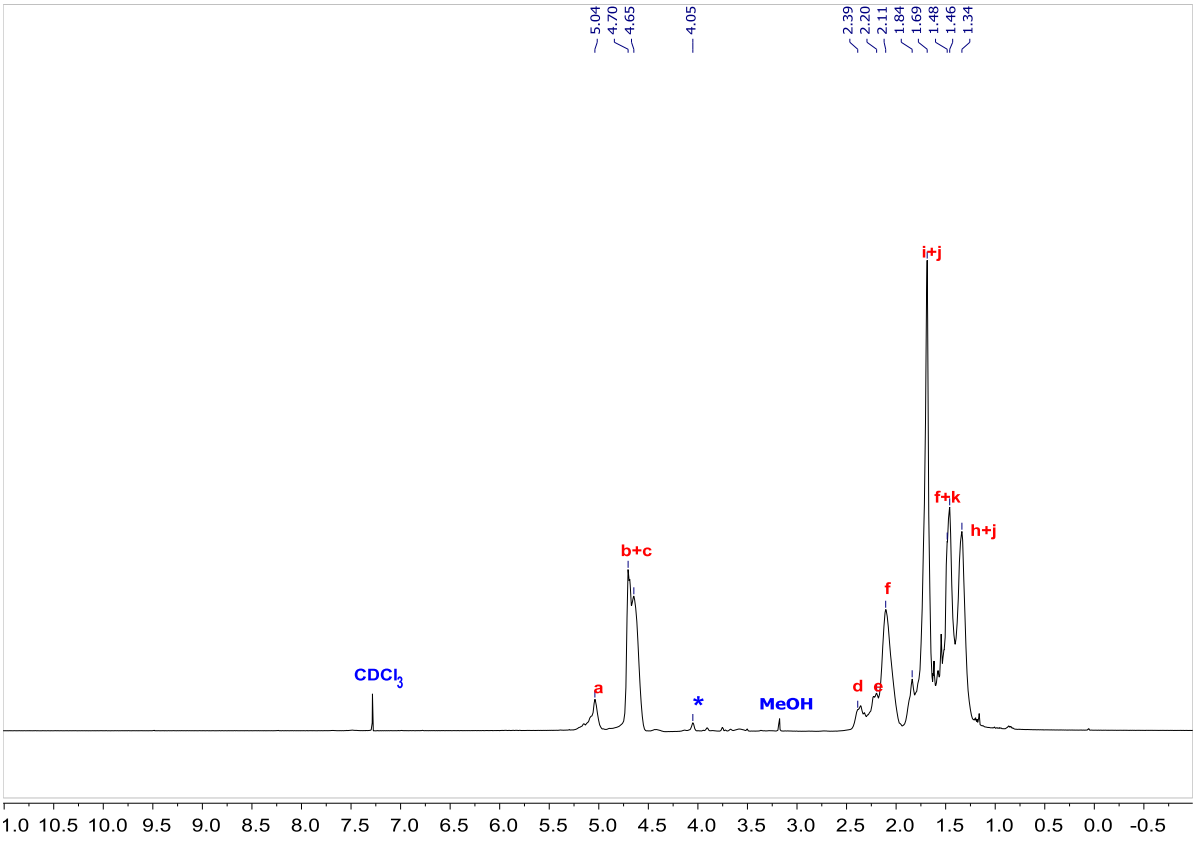
Figure S10. ^{13}C NMR spectrum of terpolymer **T-20** in $CDCl_3$ (101 MHz) at RT.

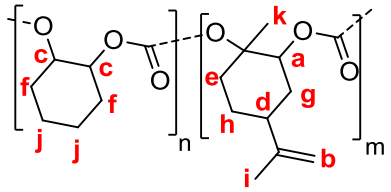




$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 MHz, RT): δ = 153.8 (C_q, C=O^{CHO}), 153.3 (C_q, C=O^{CHO}), 152.1-151.9 (C_q, C=O^{LO}), 148.8-148.4 (C_q, C=CH$_2^{LO}$), 109.2 (C=CH$_2^{LO}$), 81.7 (C_q, OC^{LO}), 77.2-76.4 (OCH^{CHO}), 76.0 (OCH^{LO}), 37.3 (CH^{LO}), 30.8 (CH$_2^{LO}$), 30.6 (CH$_2^{LO}$), 29.7-28.6 (CH$_2^{CHO}$), 25.8 (CH$_2^{LO}$), 23.2-22.0 (CH$_2^{CHO}$), 21.5-21.4 (CH$_3^{LO}$), 21.0-20.7 (CH$_3^{LO}$).

Figure S11. ^{1}H NMR spectrum of terpolymer **T-30** in $CDCl_3$ (400 MHz) at RT.

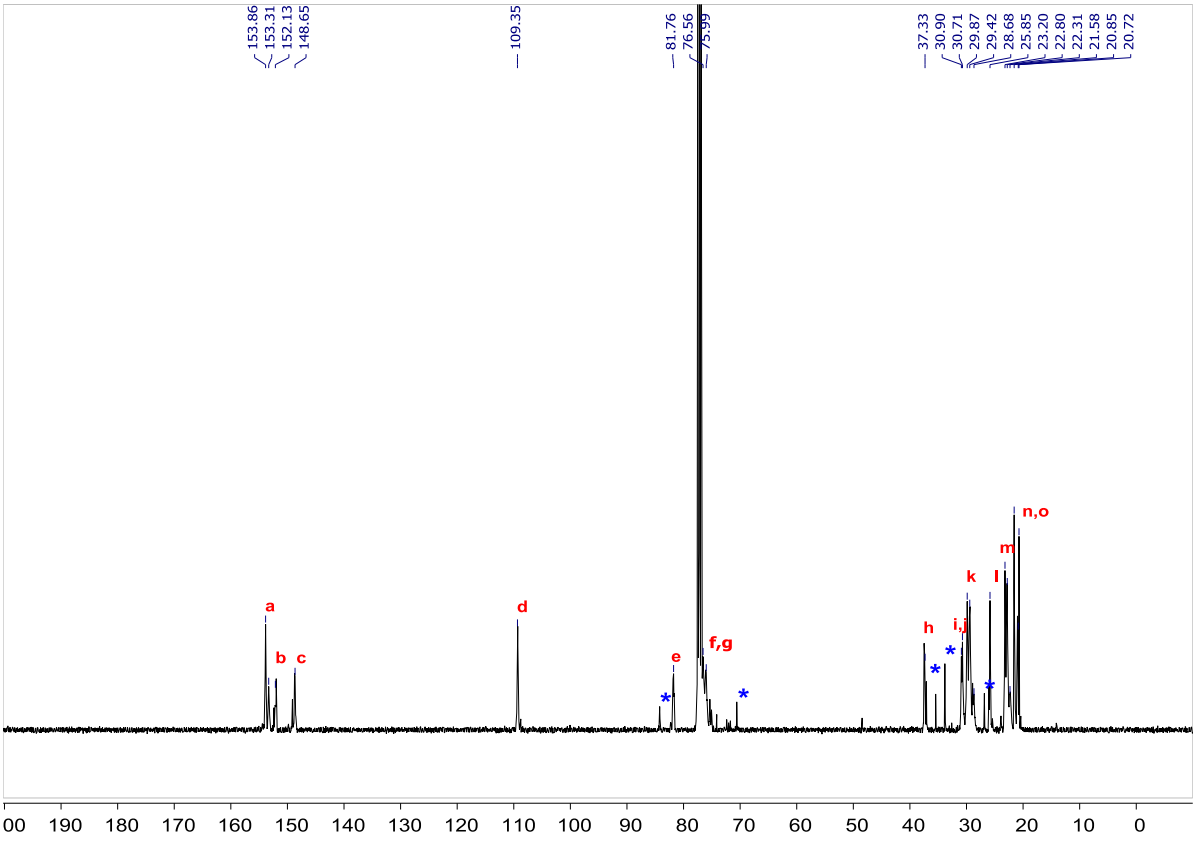


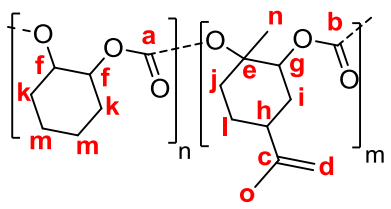


^{1}H NMR ($CDCl_3$, 400 MHz, RT): δ = 5.04 (s br, 1H^{LO}), 4.75-4.57 (m br, 2H^{CHO} + 2H^{LO}), 2.43-2.30 (m br, 1H^{LO}), 2.25-2.17 (m br, 1H^{LO}), 2.11 (m br, 2H^{CHO}), 1.90-1.56 (m br, 4H^{LO}), 1.69 (m br, 2H^{CHO} + 3H^{LO}), 1.58-1.45 (m br, 2H^{CHO} + 3H^{LO}), 1.42-1.23 (m br, 2H^{CHO} + 1H^{LO}).

* For the LO ether linkages: 4.04 ppm

Figure S12. ^{13}C NMR spectrum of terpolymer **T-30** in $CDCl_3$ (101 MHz) at RT.

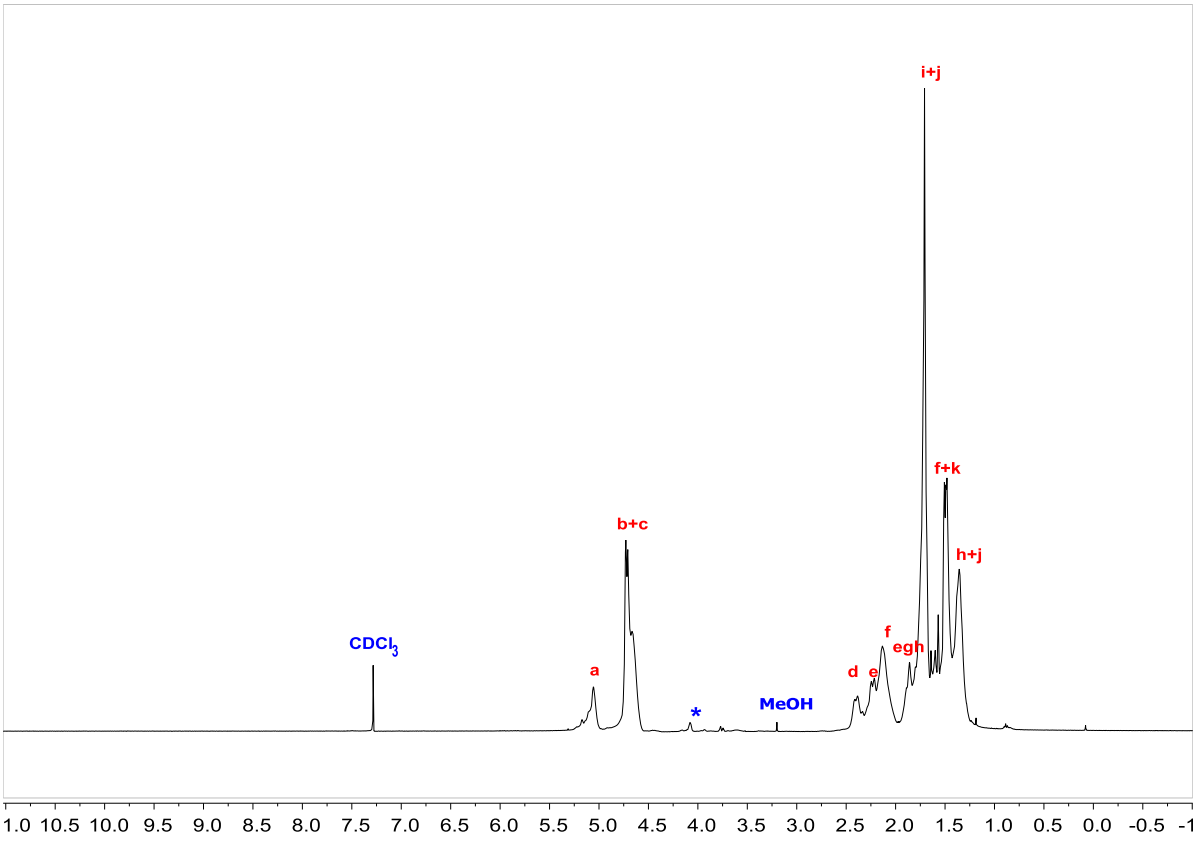


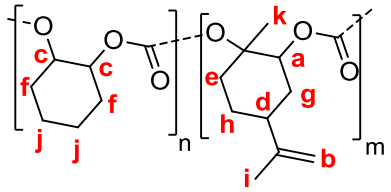


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 MHz, RT): δ = 153.8 (C_q, C=O^{CHO}), 153.3 (C_q, C=O^{CHO}), 152.1-151.9 (C_q, C=O^{LO}), 148.8-148.4 (C_q, C=CH$_2^{LO}$), 109.2 (C=CH$_2^{LO}$), 81.7 (C_q, OC^{LO}), 77.2-76.4 (OCH^{CHO}), 76.0 (OCH^{LO}), 37.3 (CH^{LO}), 30.8 (CH$_2^{LO}$), 30.6 (CH$_2^{LO}$), 29.7-28.6 (CH$_2^{CHO}$), 25.8 (CH$_2^{LO}$), 23.2-22.0 (CH$_2^{CHO}$), 21.5-21.4 (CH$_3^{LO}$), 21.0-20.7 (CH$_3^{LO}$).

* For the LO ether linkages: 84.2, 70.6, 37.1, 33.8, 26.9 ppm

Figure S13. ^{1}H NMR spectrum of terpolymer **T-40** in $CDCl_3$ (400 MHz) at RT.

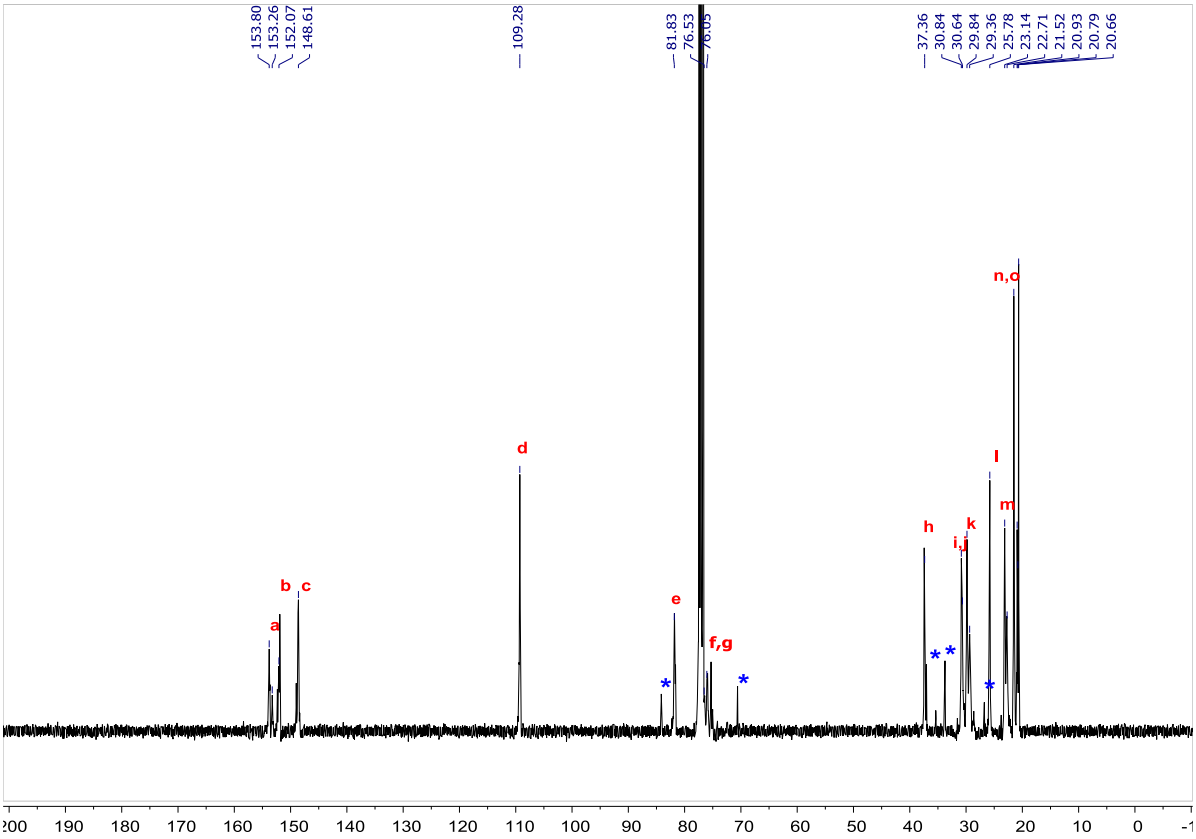


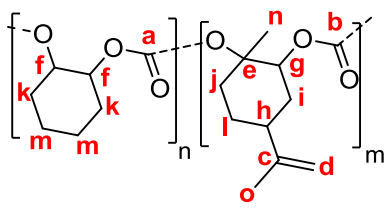


^{1}H NMR ($CDCl_3$, 400 MHz, RT): δ = 5.04 (s br, $1H_{LO}$), 4.75-4.57 (m br, $2H_{CHO}$ + $2H_{LO}$), 2.43-2.30 (m br, $1H_{LO}$), 2.25-2.17 (m br, $1H_{LO}$), 2.11 (m br, $2H_{CHO}$), 1.90-1.56 (m br, $4H_{LO}$), 1.69 (m br, $2H_{CHO}$ + $3H_{LO}$), 1.58-1.45 (m br, $2H_{CHO}$ + $3H_{LO}$), 1.42-1.23 (m br, $2H_{CHO}$ + $1H_{LO}$).

* For the LO ether linkages: 4.04 ppm

Figure S14. ^{13}C NMR spectrum of terpolymer **T-40** in $CDCl_3$ (101 MHz) at RT.

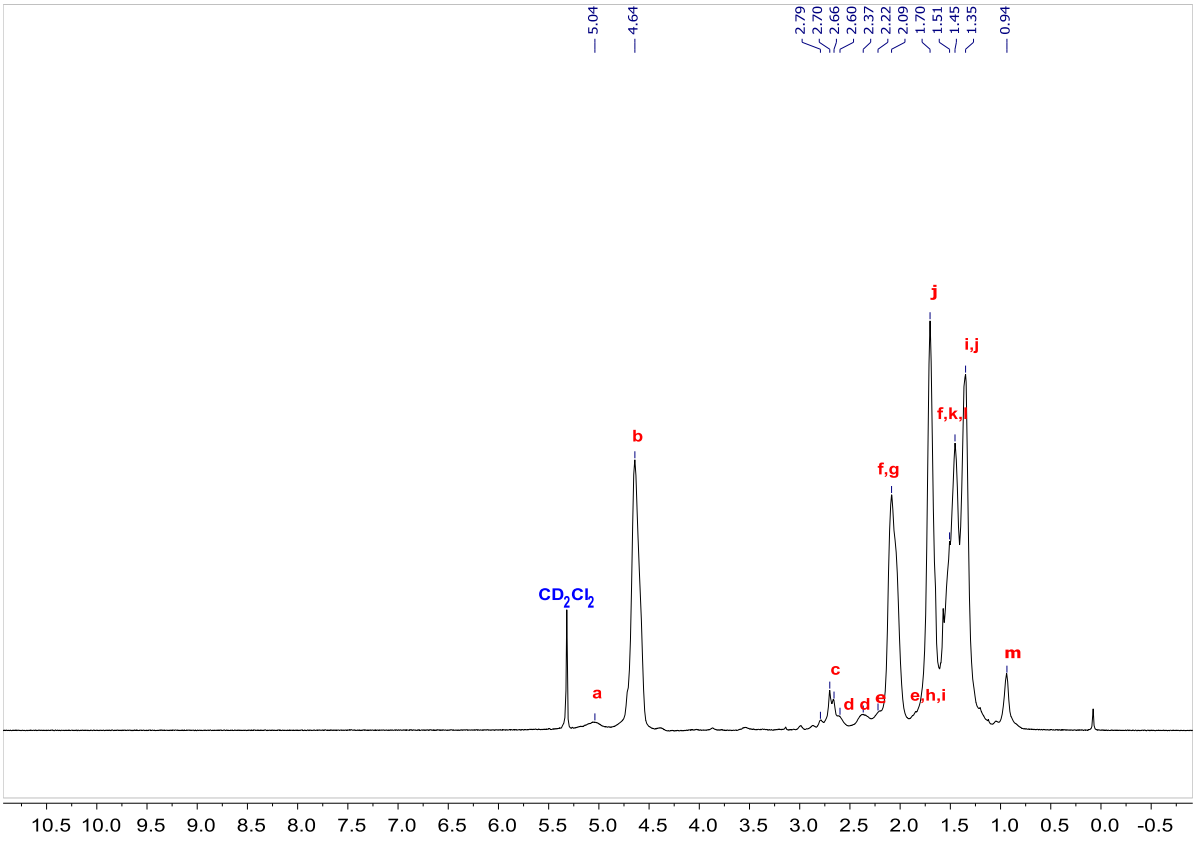


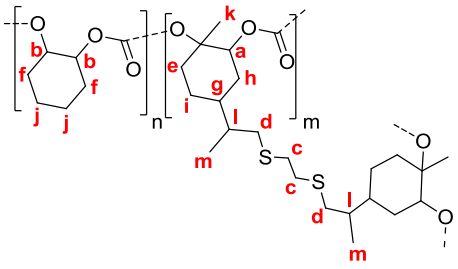


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 MHz, RT): δ = 153.8 (C_q, C=O^{CHO}), 153.3 (C_q, C=O^{CHO}), 152.1-151.9 (C_q, C=O^{LO}), 148.8-148.4 (C_q, C=CH$_2^{LO}$), 109.2 (C=CH$_2^{LO}$), 81.7 (C_q, OC^{LO}), 77.2-76.4 (OCH^{CHO}), 76.0 (OCH^{LO}), 37.3 (CH^{LO}), 30.8 (CH$_2^{LO}$), 30.6 (CH$_2^{LO}$), 29.7-28.6 (CH$_2^{CHO}$), 25.8 (CH$_2^{LO}$), 23.2-22.0 (CH$_2^{CHO}$), 21.5-21.4 (CH$_3^{LO}$), 21.0-20.7 (CH$_3^{LO}$).

* For the LO ether linkages: 84.2, 70.6, 37.1, 33.8, 26.9 ppm

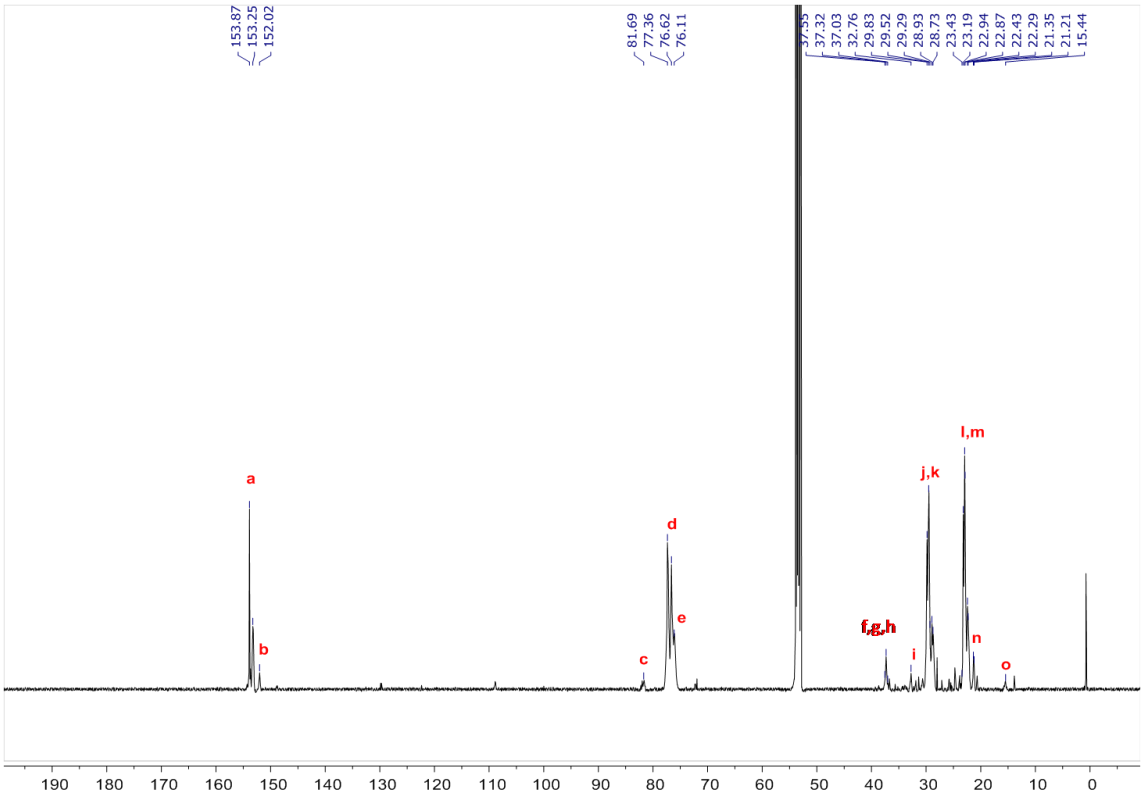
Figure S15. ^{1}H NMR spectrum of cross-linked polymer **CLP-10** in CD_2Cl_2 (400 MHz) at RT.

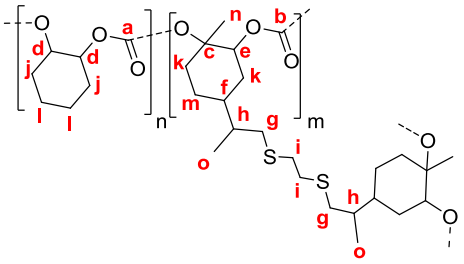




^{1}H NMR (CD_2Cl_2, 400 MHz, RT): δ = 5.12-5.00 (s br, 1H^{LO}), 4.64 (s br, 2H^{CHO}), 2.79, 2.70 and 2.66 (2s br, SCH_2, 4H), 2.60 and 2.37 (2s br, SCH_2, 4H), 2.25-2.17 (m br, 1H^{LO}), 2.09 (m br, 2H^{CHO} + 1H^{LO}), 1.87-1.60 (m br, 5H^{LO}), 1.71 (m br, 2H^{CHO}), 1.57-1.40 (m br, 2H^{CHO} + 3H^{LO} + 1C*H*), 1.38-1.30 (m br, 2H^{CHO} + 1H^{LO}), 0.94 (s br, CH_3).

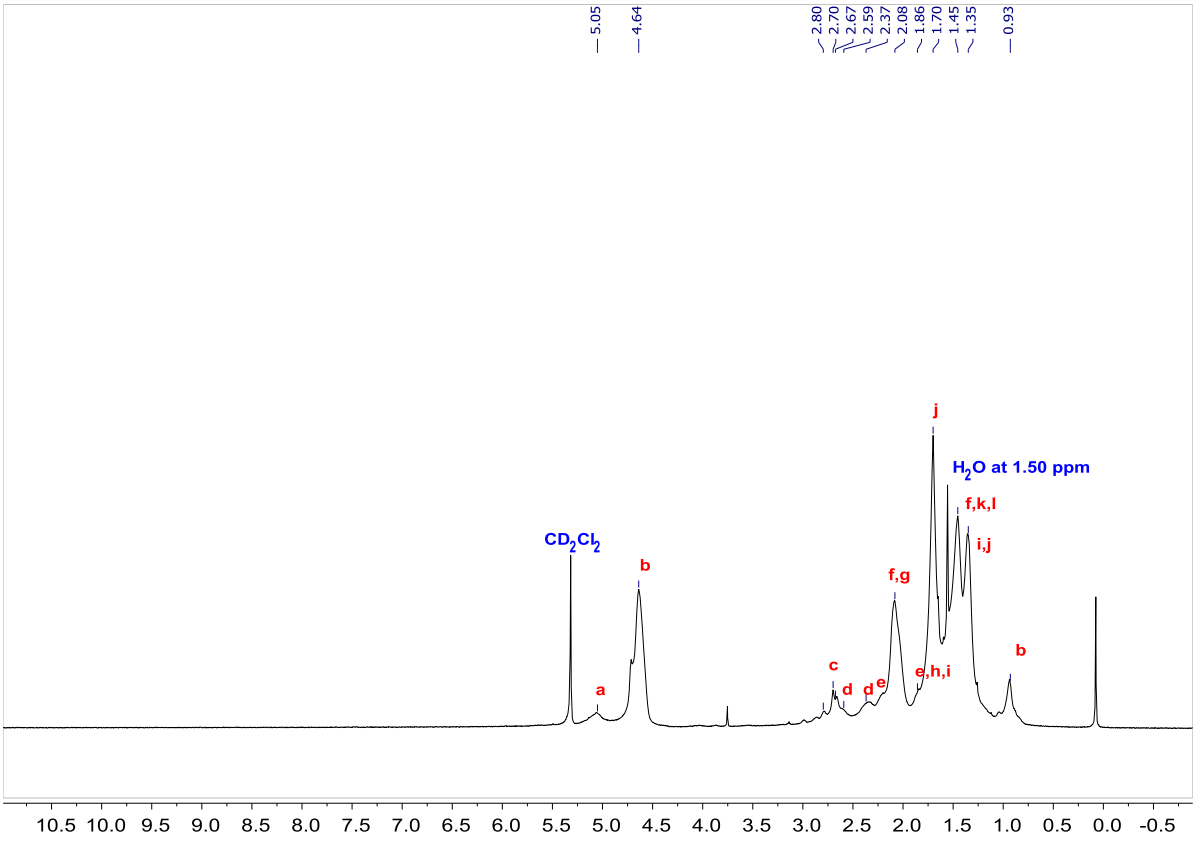
Figure S16. ^{13}C NMR spectrum of cross-linked polymer **CLP-10** in CD_2Cl_2 (101 MHz) at RT.

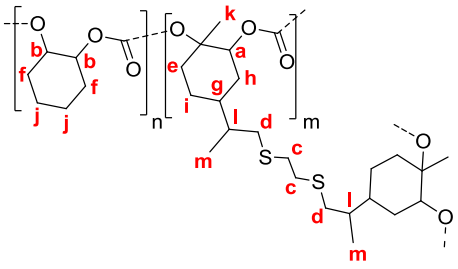




$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 400 MHz, RT): δ = 153.8 (C_q, C=O^{CHO}), 153.3-153.1 (C_q, C=O^{CHO}), 152.0 (C_q, C=O^{LO}), 81.7 (C_q, OC^{LO}), 77.6-76.4 (OCH^{CHO}), 76.3-75.7 (OCH^{LO}), 37.3-37.1 (SCH$_2$CH, SCH$_2$$CH, CHC$H^{LO}), 32.8 (S$CH_2$$CH_2$S), 30.0-29.2 ($CH_2^{CHO}$, CH$_2^{LO}$), 29.0-28.5 (CH$_2^{LO}$), 23.3-22.1 (CH$_2^{CHO}$, CH$_2^{LO}$), 21.5-21.1 (CH$_3^{LO}$), 15.4 (CH$_3^{LO}$).

Figure S17. ^{1}H NMR spectrum of cross-linked polymer **CLP-20** in CD_2Cl_2 (400 MHz) at RT.

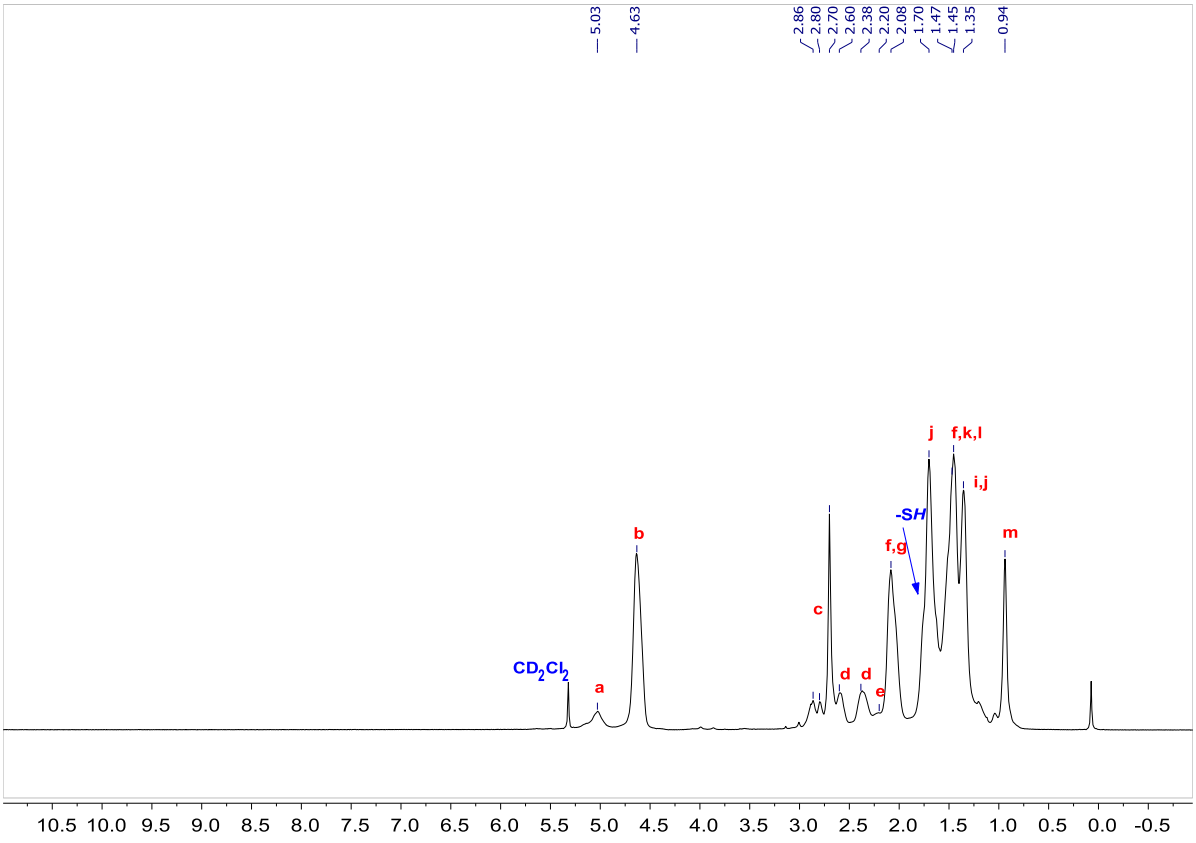


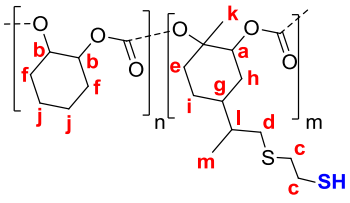


^{1}H NMR (CD_2Cl_2, 400 MHz, RT): δ = 5.12-5.00 (s br, 1H^{LO}), 4.64 (s br, 2H^{CHO}), 2.79, 2.70 and 2.66 (2s br, SCH_2, 4H), 2.60 and 2.37 (2s br, SCH_2, 4H), 2.25-2.17 (m br, 1H^{LO}), 2.09 (m br, 2H^{CHO} + 1H^{LO}), 1.87-1.60 (m br, 5H^{LO}), 1.71 (m br, 2H^{CHO}), 1.57-1.40 (m br, 2H^{CHO} + 3H^{LO} + 1CH), 1.38-1.30 (m br, 2H^{CHO} + 1H^{LO}), 0.94 (s br, CH_3).

* A ^{13}C NMR spectrum of cross-linked polymer **CLP-20** was not possible as the sample formed a gel and was not enough soluble.

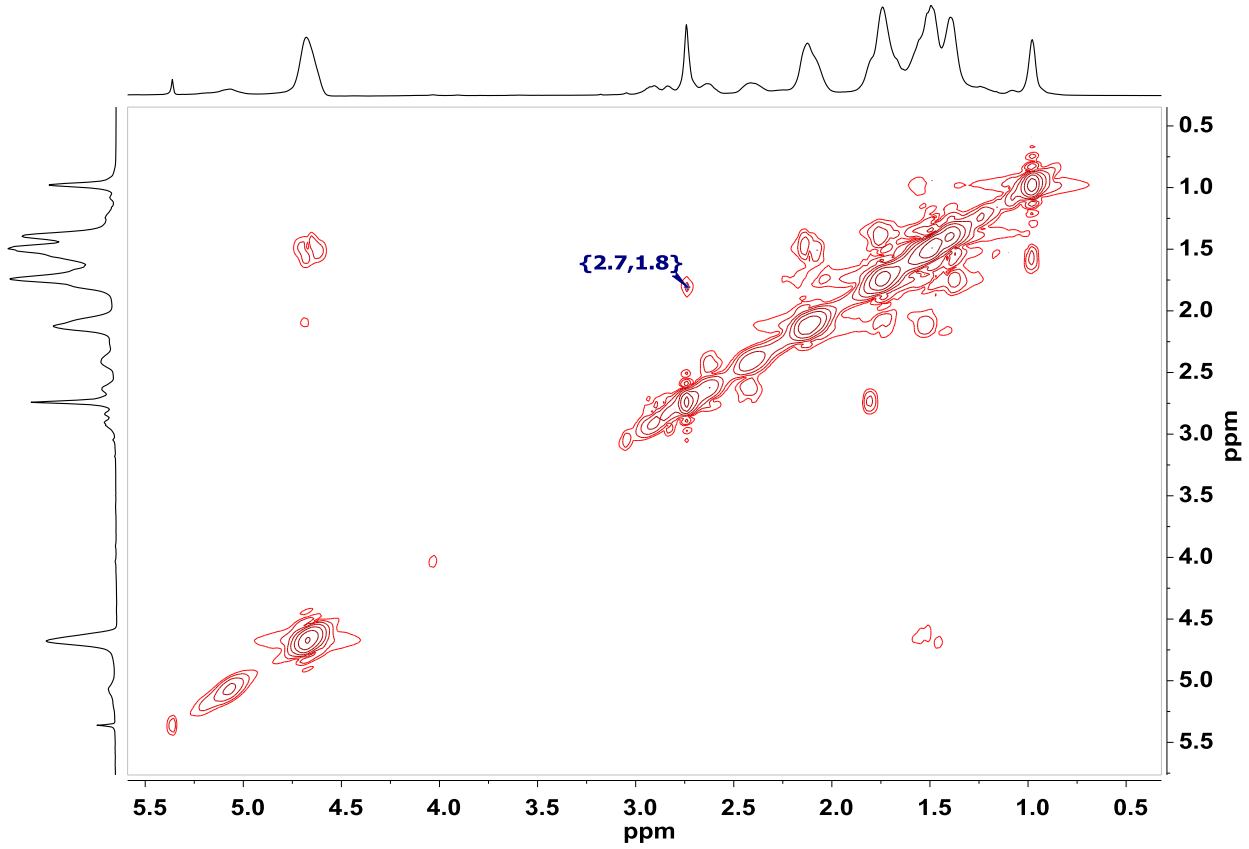
Figure S18. ^{1}H NMR spectrum of cross-linked polymer **CLP-20a** in CD_2Cl_2 (400 MHz) at RT.





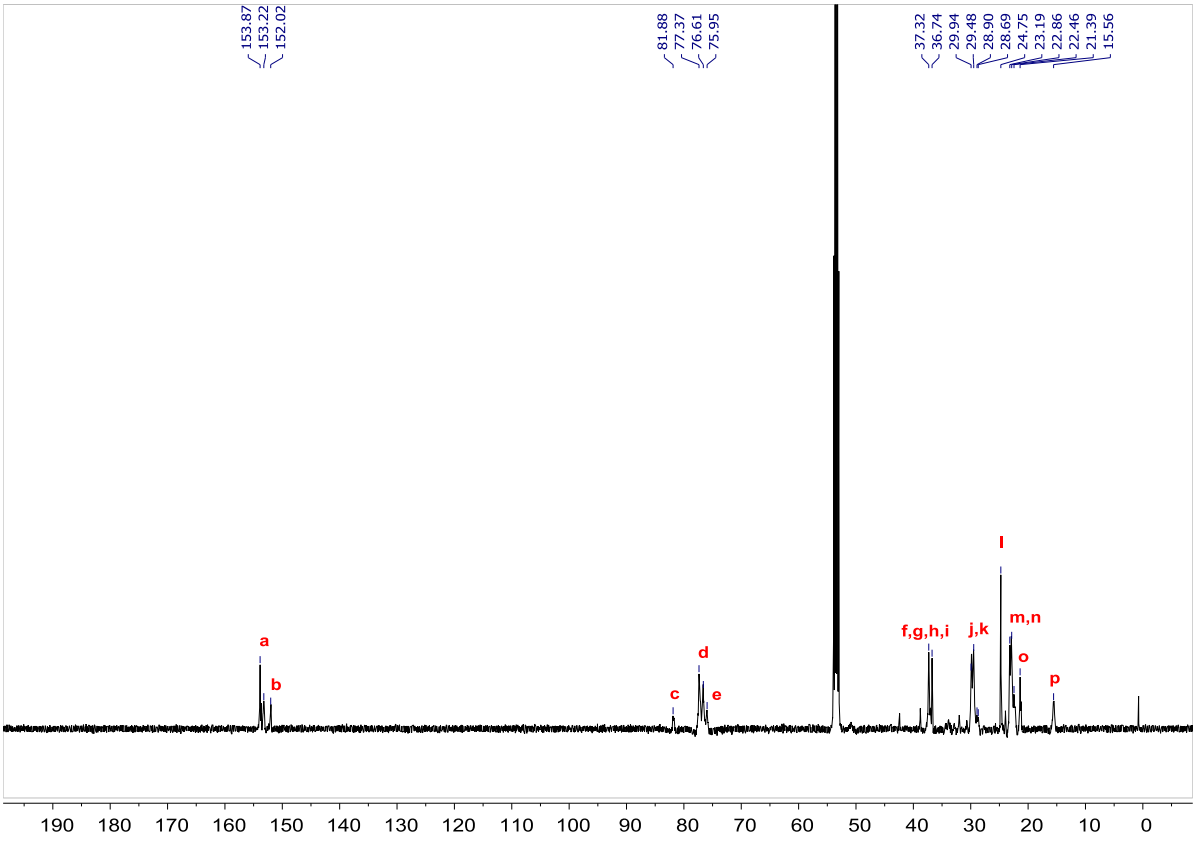
^{1}H NMR (CD_2Cl_2, 400 MHz, RT): δ = 5.12-5.00 (s br, 1H^{LO}), 4.63 (s br, 2H^{CHO}), 2.86, 2.80 and 2.70 (2s br, SCH_2, 4H), 2.60 and 2.38 (2s br, SCH_2, 4H), 2.25-2.17 (m br, 1H^{LO}), 2.08 (m br, 2H^{CHO} + 1H^{LO}), 1.87-1.60 (m br, 1H^{SH}, 5H^{LO}), 1.70 (m br, 2H^{CHO}), 1.57-1.40 (m br, 2H^{CHO} + 3H^{LO} + 1CH), 1.39-1.30 (m br, 2H^{CHO} + 1H^{LO}), 0.94 (s br, CH_3).

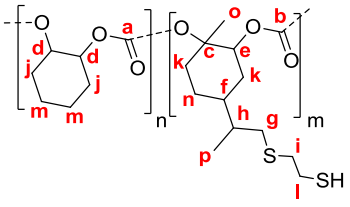
Figure S19. COSY spectrum for cross-linked polymer **CLP-20a** in CD_2Cl_2 at RT.



*Correlation between $–SCH_2CH_2SH$ (at 2.7 ppm) and –S*H* (at 1.8 ppm).

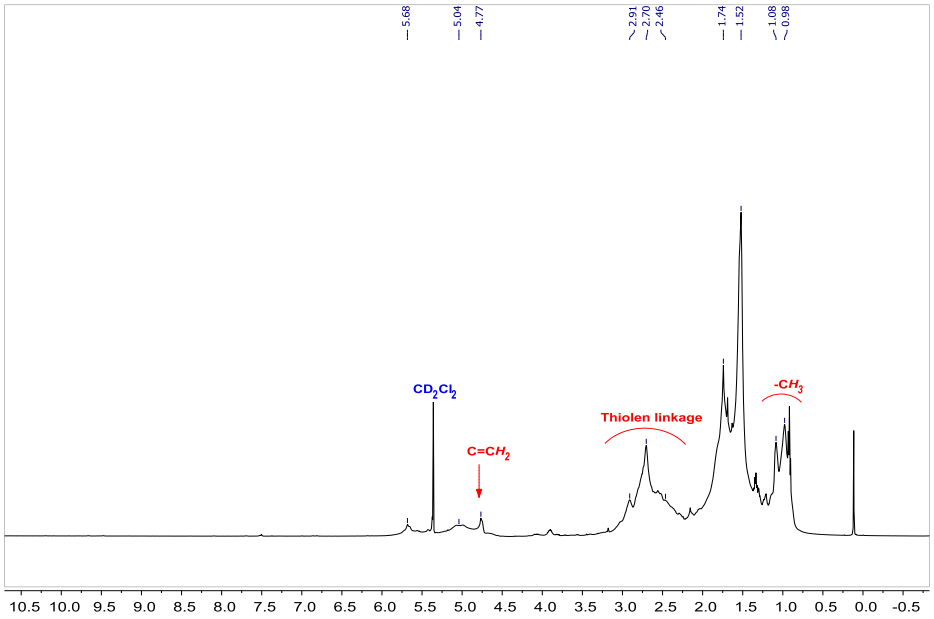
Figure S20. ^{13}C NMR spectrum of cross-linked polymer **CLP-20a** in CD_2Cl_2 (101 MHz) at RT.





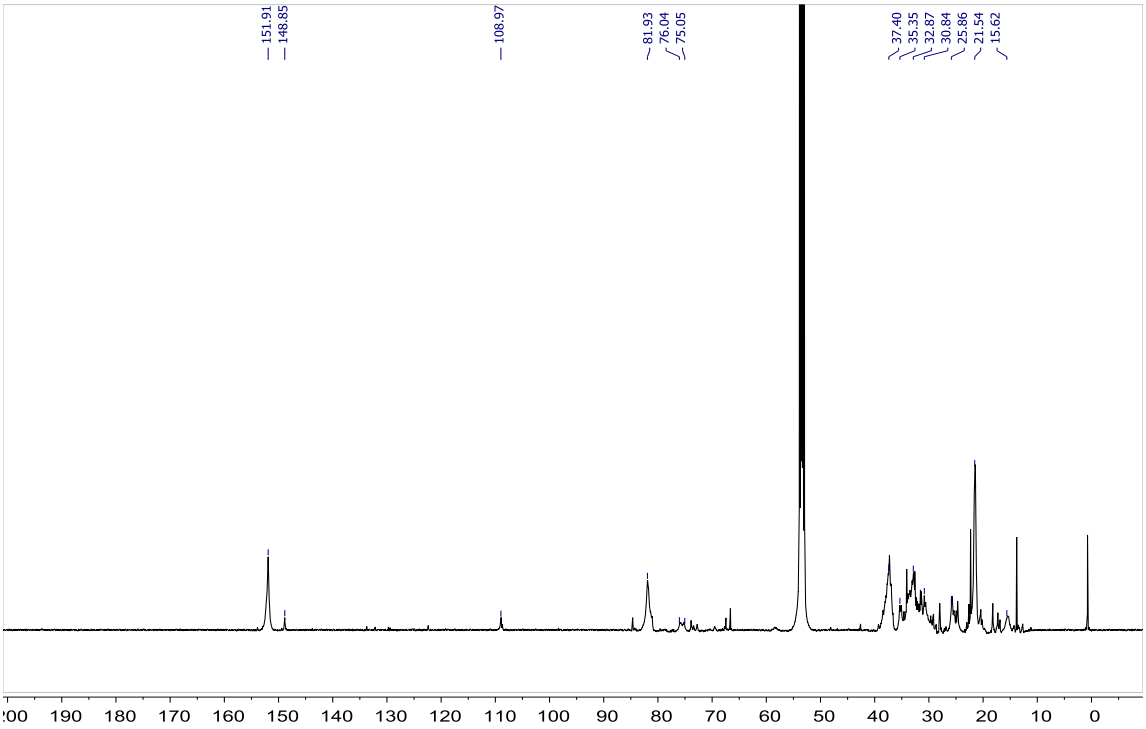
$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 400 MHz, RT): δ = 153.9 (C_q, C=O^{CHO}), 153.4-153.1 (C_q, C=O^{CHO}), 152.0 (C_q, C=O^{LO}), 81.9 (C_q, OC^{LO}), 77.6-76.4 (OCH^{CHO}), 76.2-75.7 (OCH^{LO}), 37.6-37.1 (SCH_2CH, SCH$_2$$CH, CHCH^{LO}$), 36.8 (S$CH_2CH_2$SH), 30.1-29.2 ($CH_2^{CHO}$, CH_2^{LO}), 29.0-28.5 (CH_2^{LO}), 24.8 (SCH$_2$$CH_2$SH), 23.3-22.1 ($CH_2^{CHO}$, CH_2^{LO}), 21.5-21.1 (CH_3^{LO}), 15.6 (CH_3^{LO}).

Figure S21. ^{1}H NMR spectrum of cross-linked polymer **CLP-100b** in CD_2Cl_2 (400 MHz) at RT.



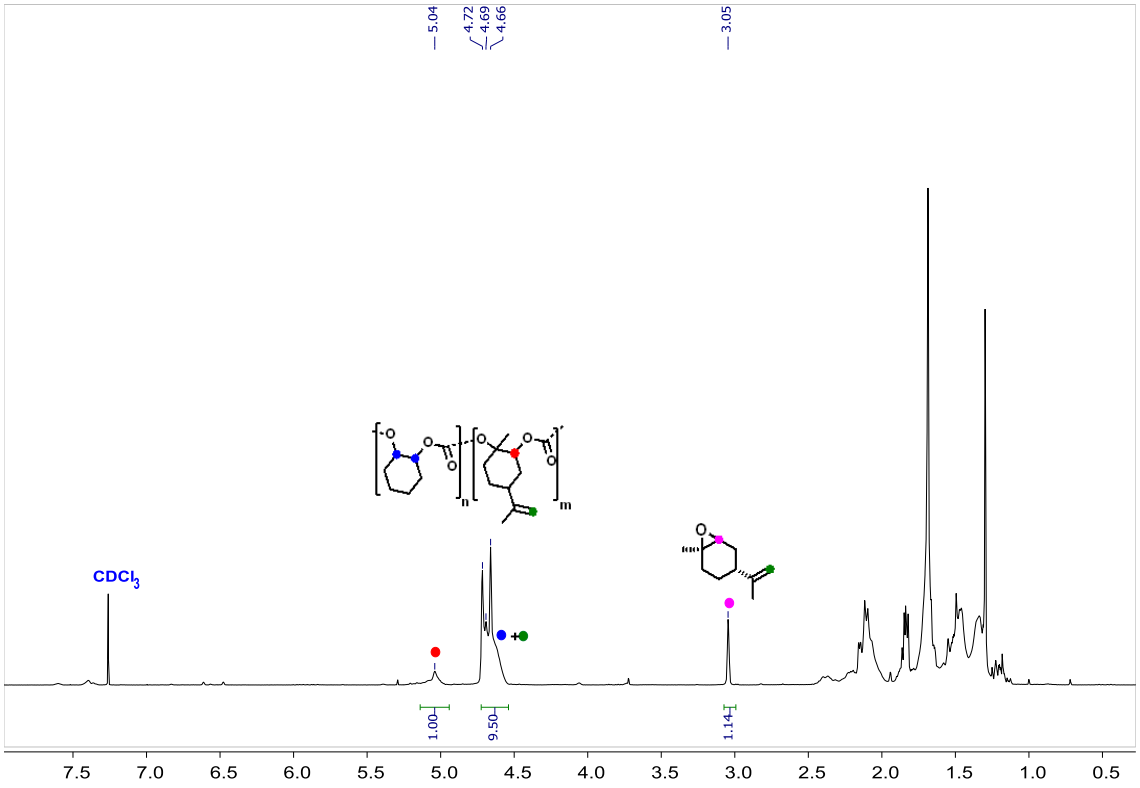
*Note that evidence for the thiolene reaction is provided by ^{1}H NMR: the virtual disappearance of the olefinic protons at 4.77 ppm, and the appearance of a new broad peak assigned to dithiol linkages (−SCH_2CH_2S− and −SCH_2−C) around 2.70 ppm, and new methylene protons at 0.98 ppm (−CH_3) are observed.

Figure S22. ^{13}C NMR spectrum of cross-linked polymer **CLP-100b** in CD_2Cl_2 (101 MHz) at RT.



*Note that evidence for the thiolene reaction is provided by the virtual disappearance of the quaternary and secondary carbon peaks pertinent to the olefin groups at 148.9 and 108.9 ppm in the ^{13}C NMR spectrum.

Figure S23. ^{1}H NMR spectrum of the crude reaction mixture after 48 h (400 MHz, RT, $CDCl_3$).



Terpolymer **T-30** containing ~28 % of LO: Reaction conditions: 1:1 ratio of CHO and LO (10 mmol in total), **Al^{Me}** = 0.50 mol %, PPNCl = 0.25 mol %, $p(CO_2)$º = 15 bar, neat, T = 40ºC. Note that the OC*H* protons for CHO at 3.12 ppm were no longer observed at the end of the process.

Figure S24. Comparative ^{1}H NMR spectra for CHO/CO_2 copolymer (blue line), $CHO/LO/CO_2$ terpolymer (green line) and LO/CO_2 copolymer (red line) at 400 MHz, RT in $CDCl_3$.

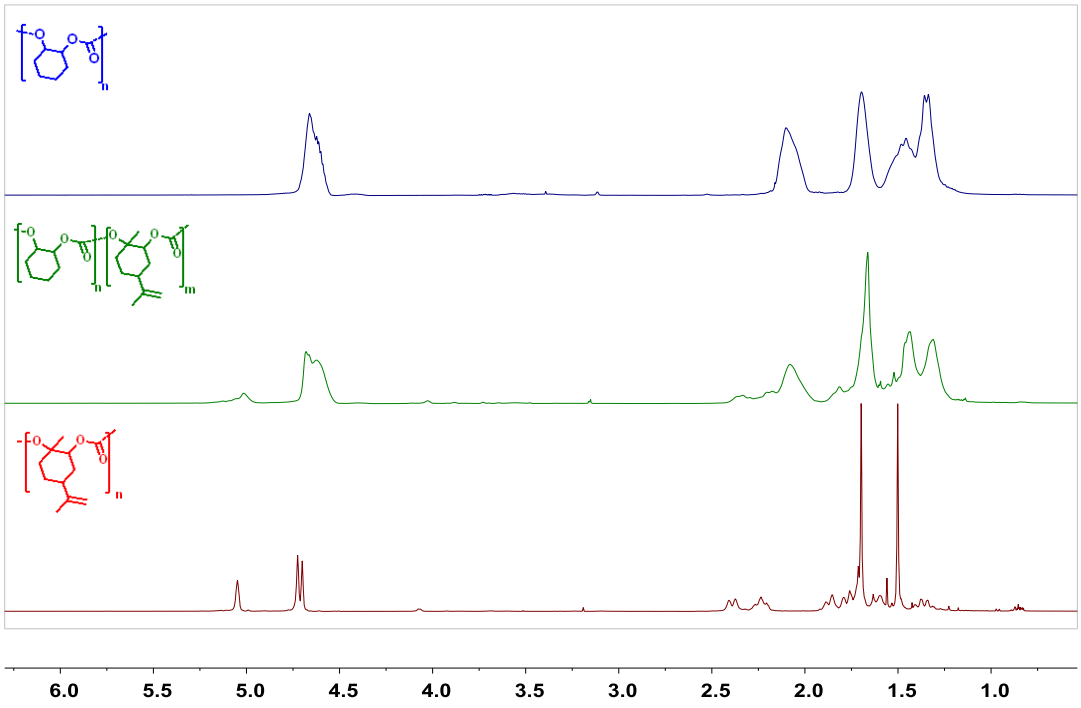


Figure S25. Comparative ^{13}C NMR spectra for **T-10** (red line) and **CLP-10** (green line) at 400 MHz, RT in CD_2Cl_2.

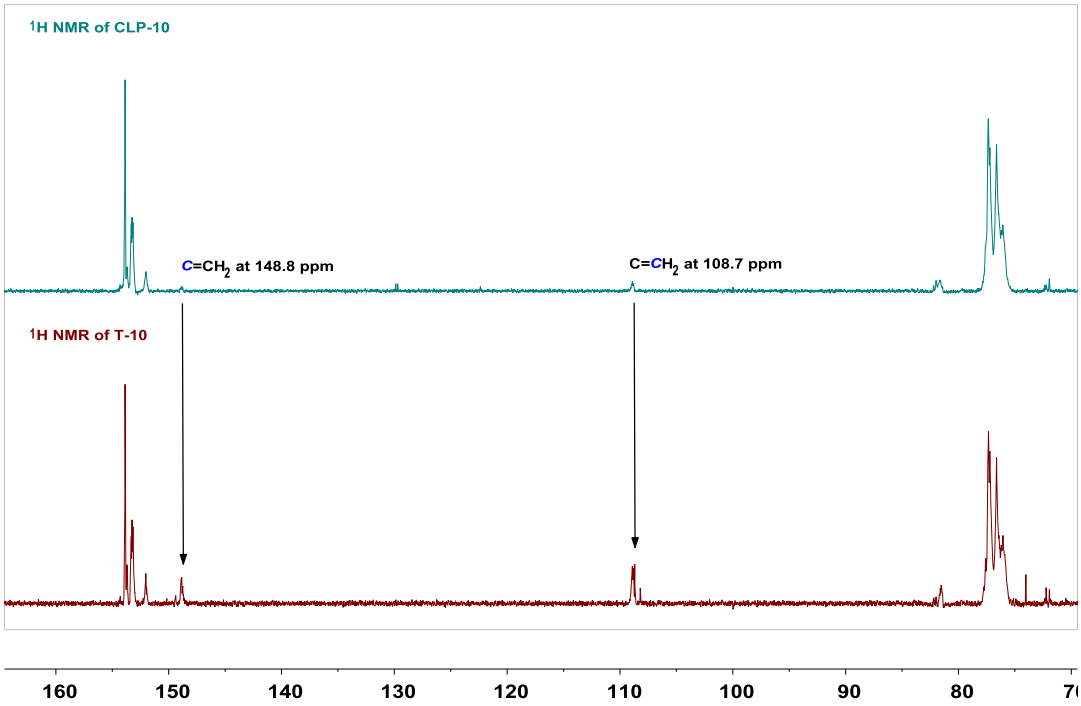
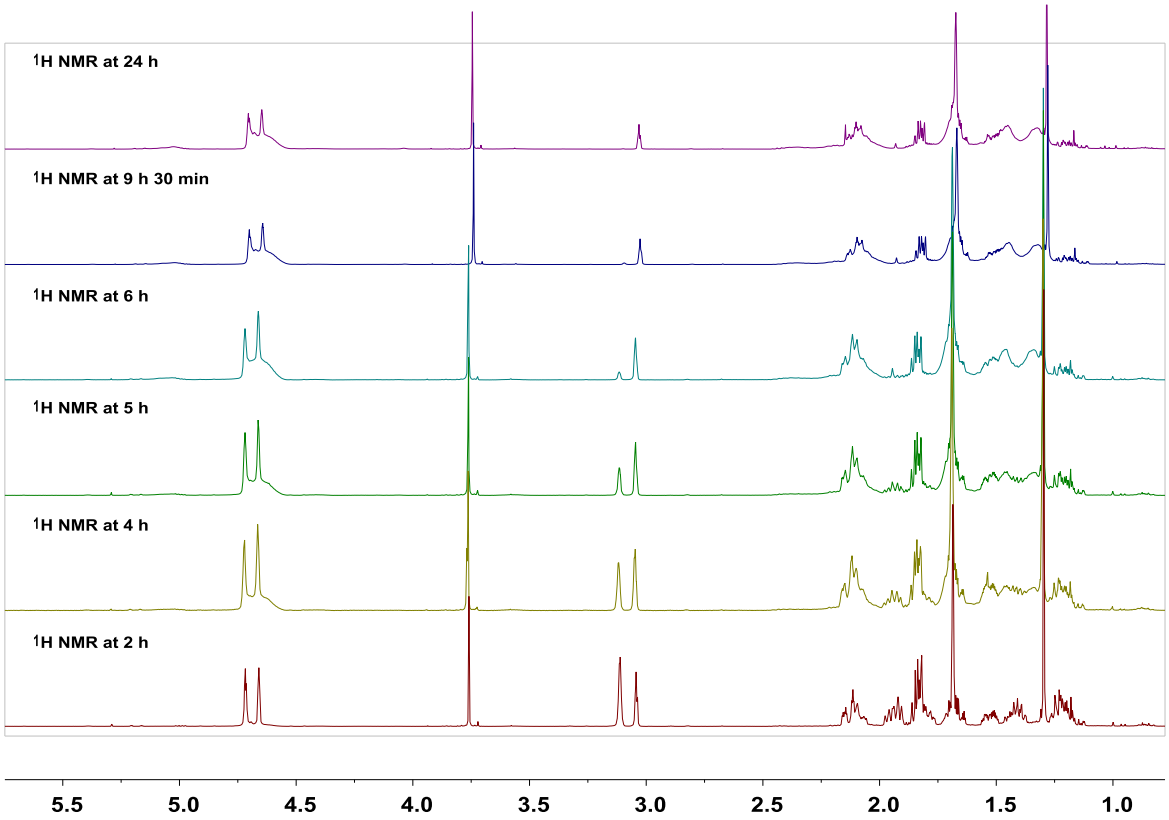


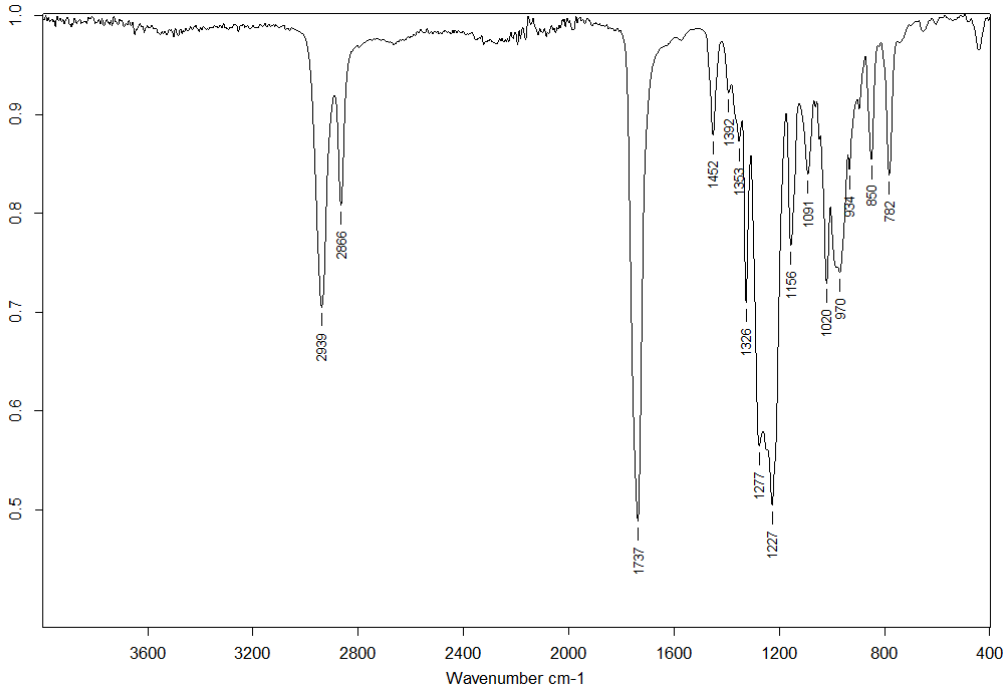
Figure S26. Comparative ^{1}H NMR spectra for the terpolymerization process after different time intervals (400 MHz, RT, $CDCl_3$).



Reaction conditions: 1:1 ratio of CHO and LO (3.5 mmol in total), cat. **Al^{Me}** = 0.50 mol %, PPNCl = 0.25 mol %, $p(CO_2)^o$ = 15 bar, neat, T = 40ºC. Polycarbonate yield, and CHO and LO conversions were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,4-dimethoxybezene as internal standard (δ = 3.76 ppm).

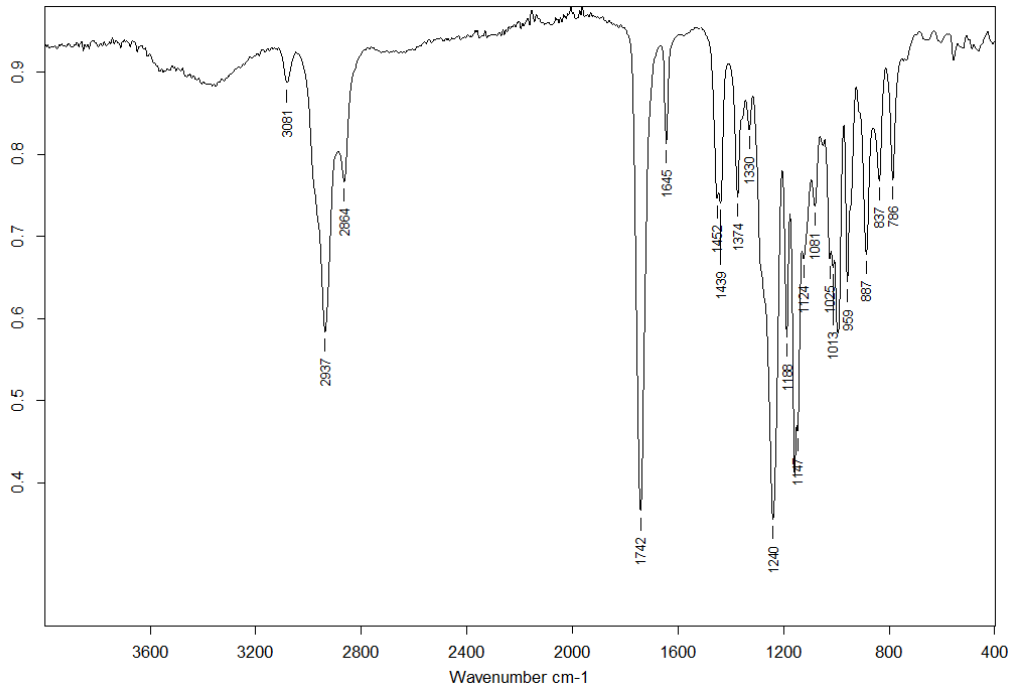
IR SPECTRA:

Figure S27. IR spectrum of CHO/CO_2 copolymer **P-0**.



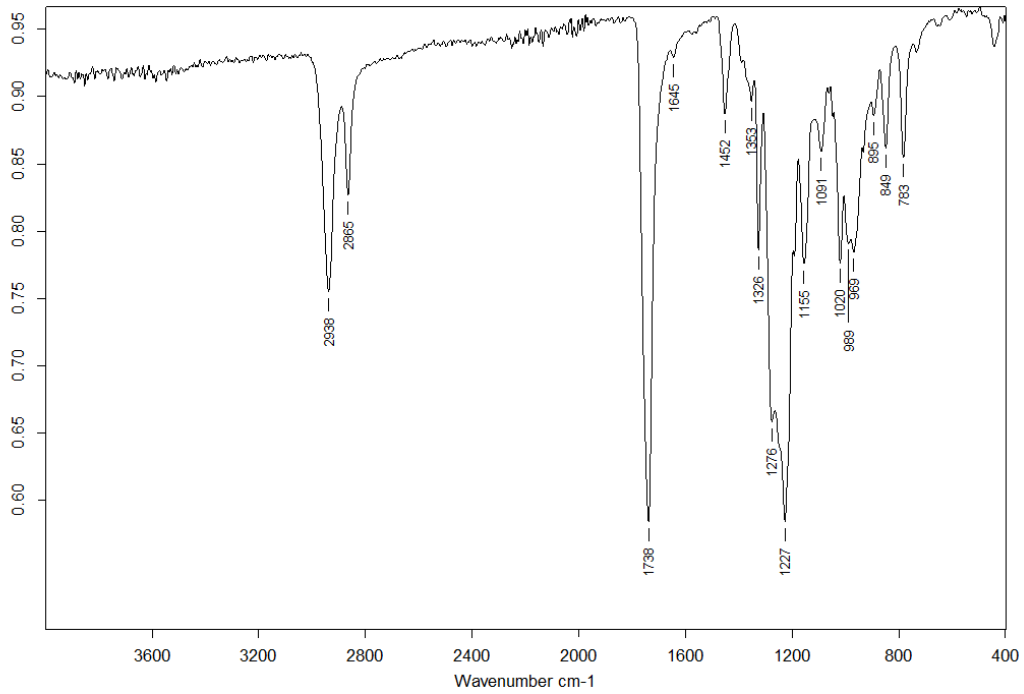
IR (neat, cm^{-1}): 1737 (C=O)

Figure S28. IR spectrum of LO/CO_2 copolymer **P-100**.



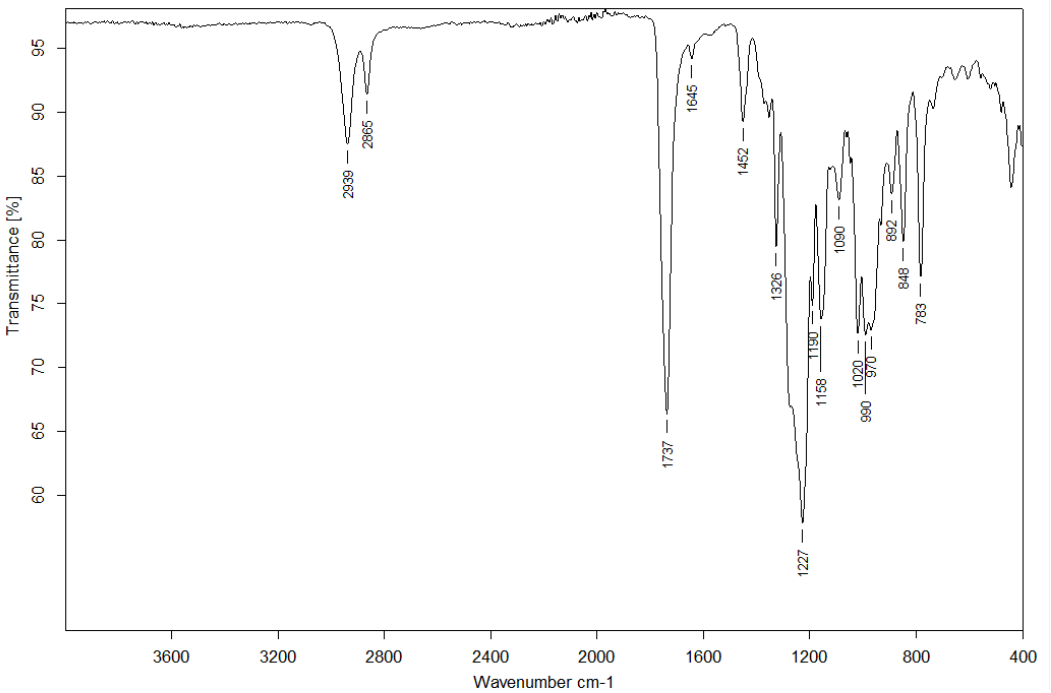
IR (neat, cm^{-1}): 1742 (C=O), 1645 (C=C), 887 (=C−H), 837 (=C−H).

Figure S29. IR spectrum of **T-10**.



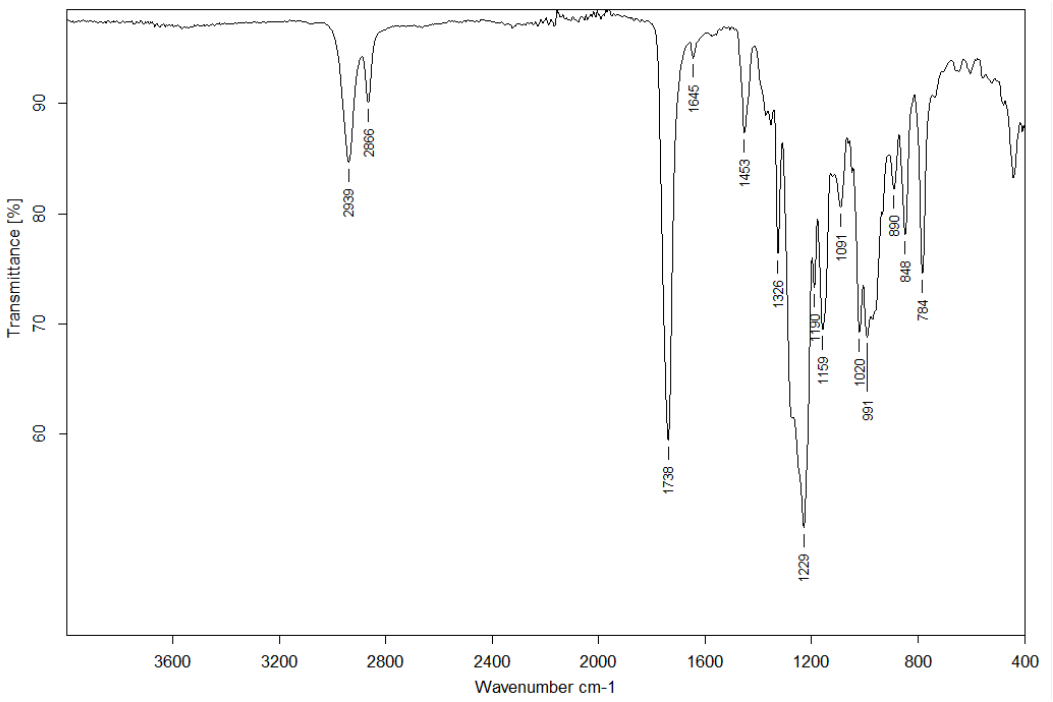
IR (neat, cm^{-1}): 1738 (C=O), 1645 (C=C), 895 (=C−H).

Figure S30. IR spectrum of **T-20**.



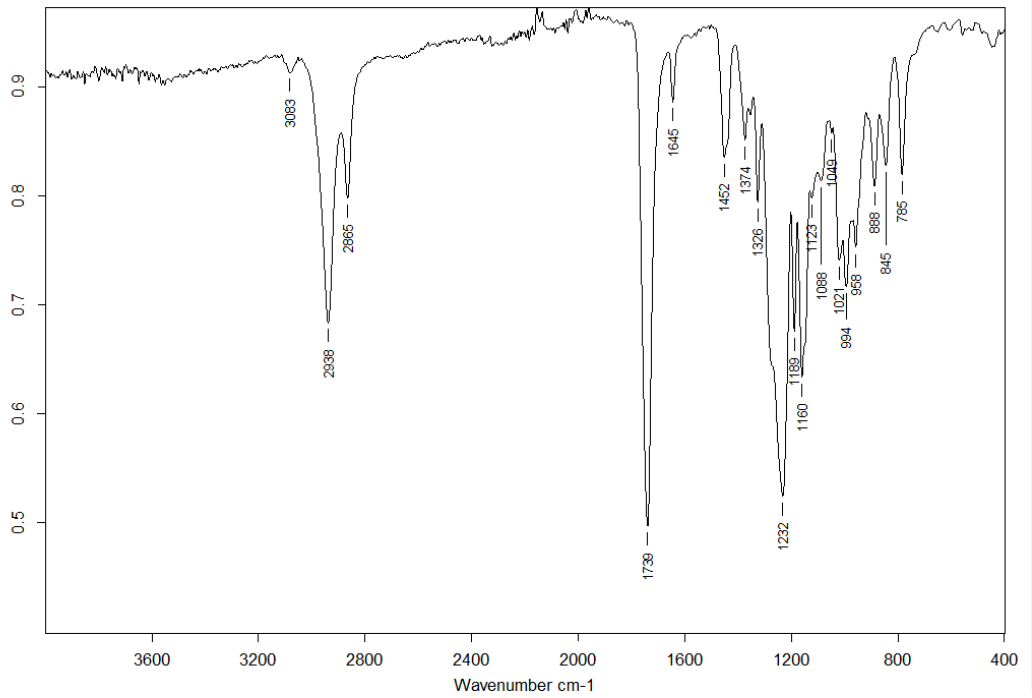
IR (neat, cm^{-1}): 1737 (C=O), 1645 (C=C), 892 (=C−H).

Figure S31. IR spectrum of **T-30**.



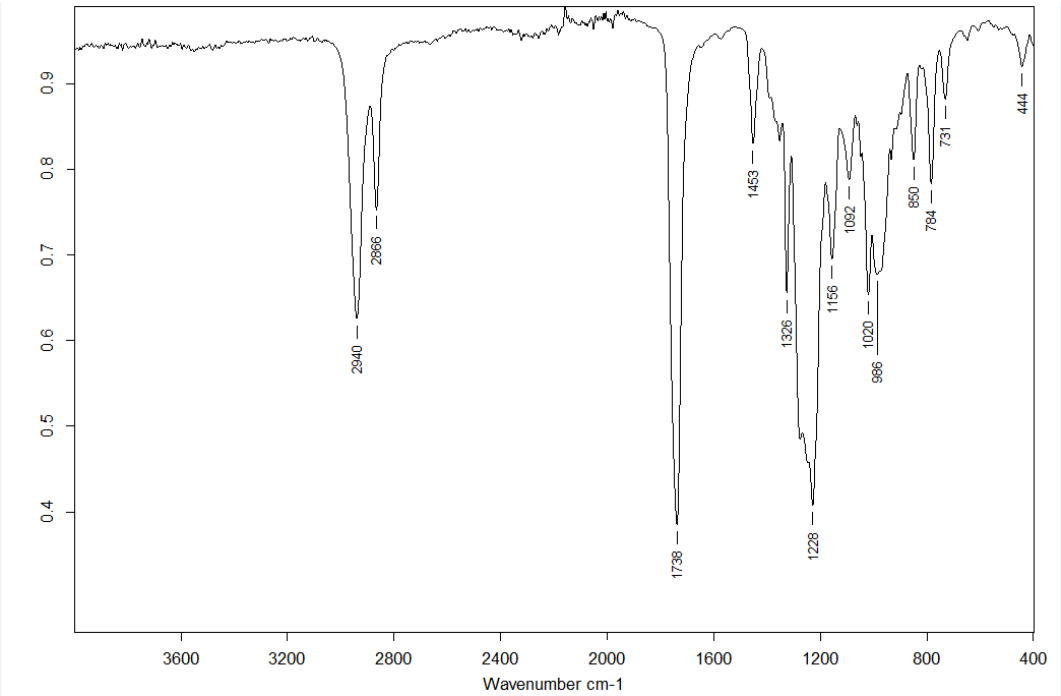
IR (neat, cm^{-1}): 1738 (C=O), 1645 (C=C), 890 (=C−H).

Figure S32. IR spectrum of **T-40**.



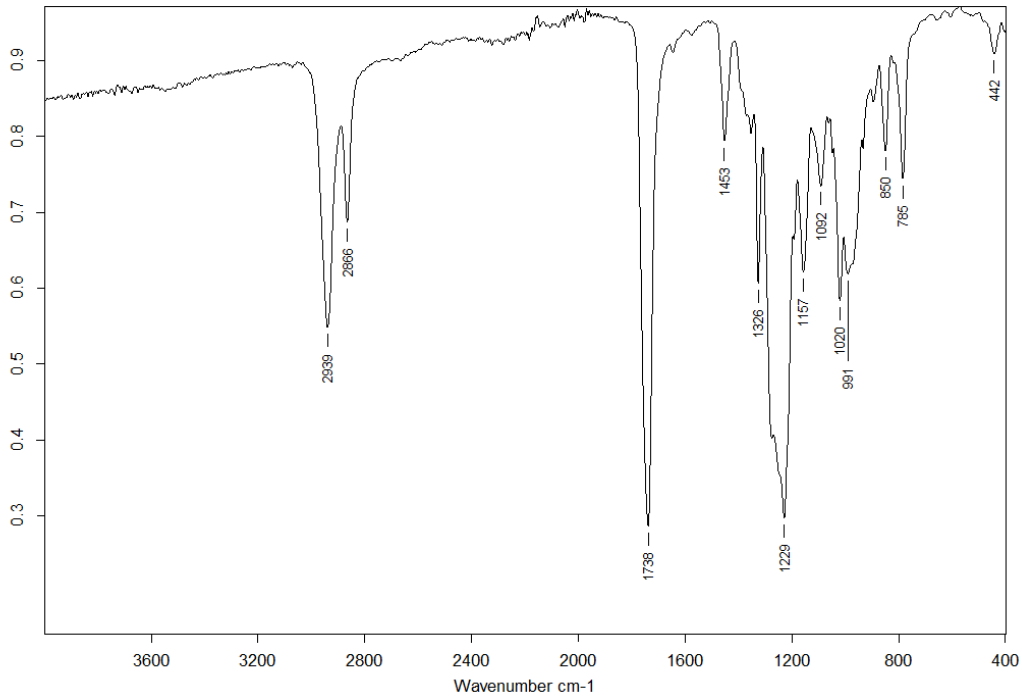
IR (neat, cm^{-1}): 1739 (C=O), 1645 (C=C), 888 (=C−H).

Figure S33. IR spectrum of **CLP-10**.



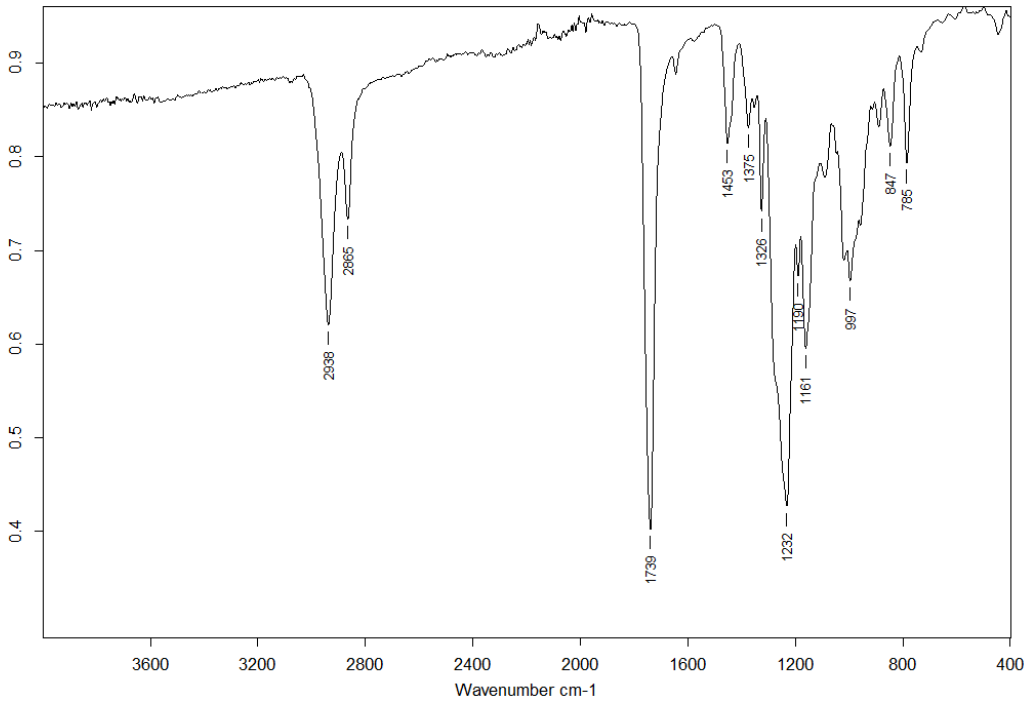
IR (neat, cm^{-1}): 1738 (C=O).

Figure S34. IR spectrum of **CLP-20**.



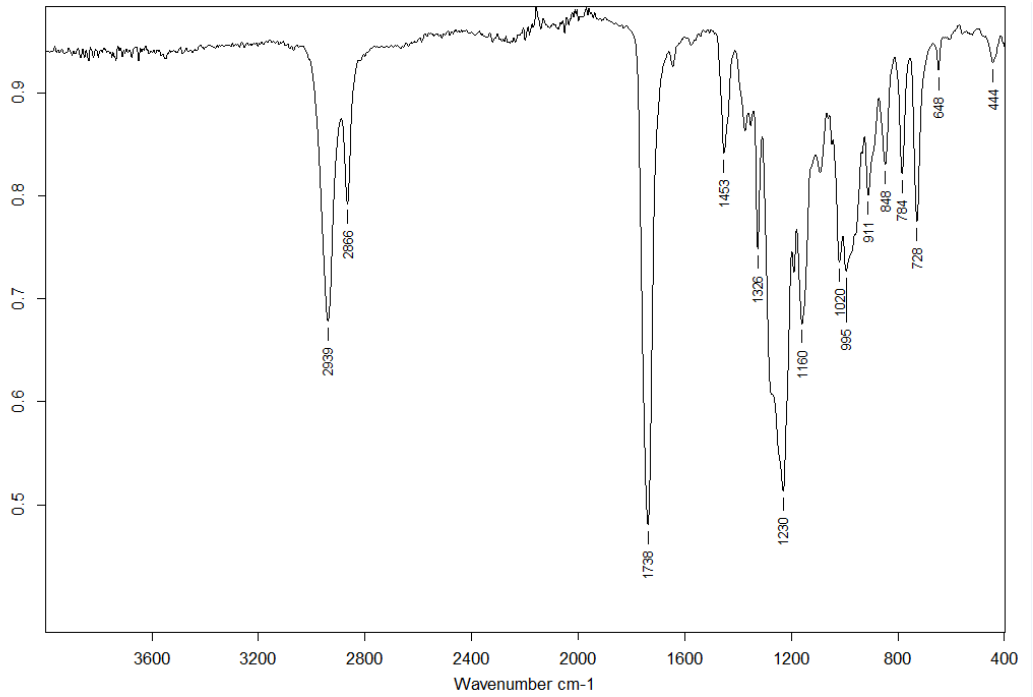
IR (neat, cm^{-1}): 1738 (C=O).

Figure S35. IR spectrum of **CLP-30**.



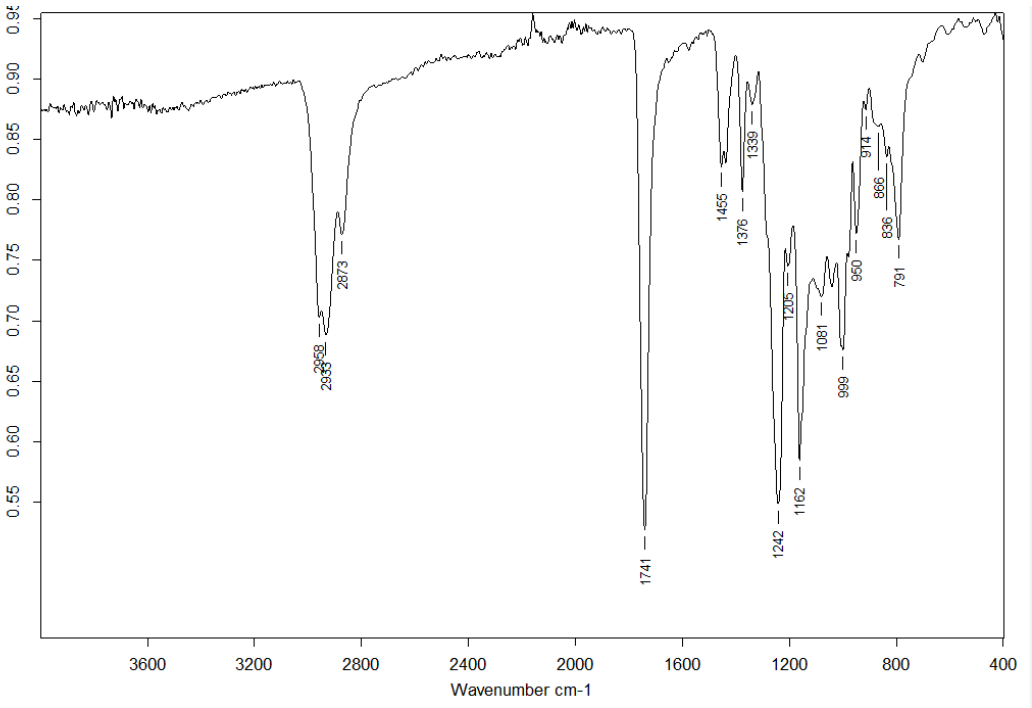
IR (neat, cm^{-1}): 1739 (C=O).

Figure S36. IR spectrum of **CLP-40**.



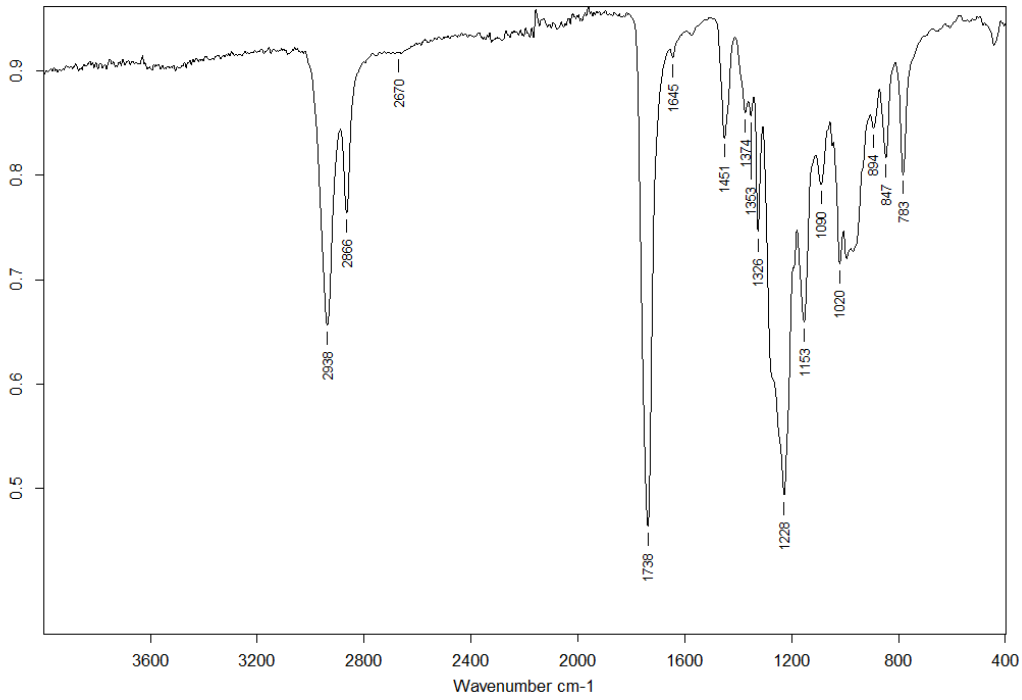
IR (neat, cm^{-1}): 1738 (C=O).

Figure S37. IR spectrum of **CLP-100**.



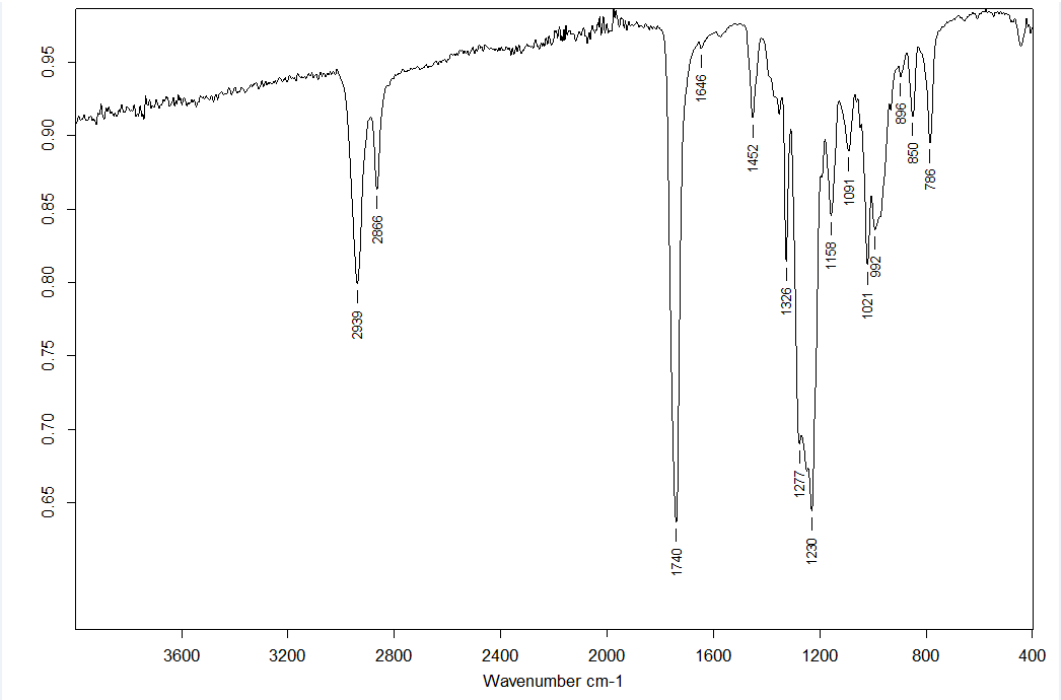
IR (neat, cm^{-1}): 1741 (C=O).

Figure S38. IR spectrum of **CLP-20a**.



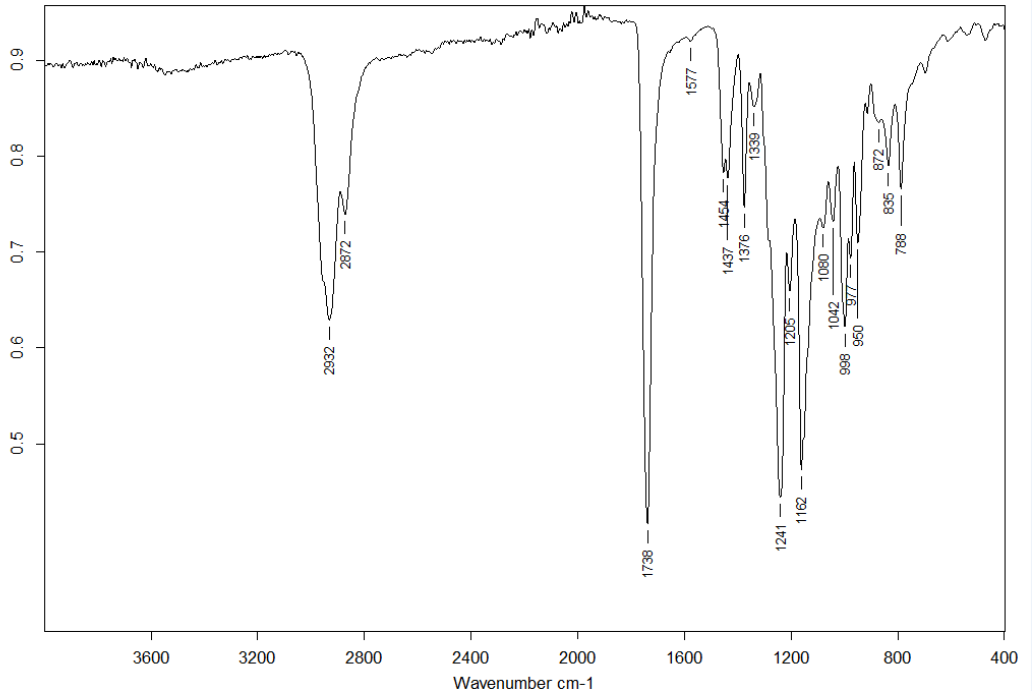
IR (neat, cm^{-1}): 1738 (C=O).

Figure S39. IR spectrum of **CLP-20d**.



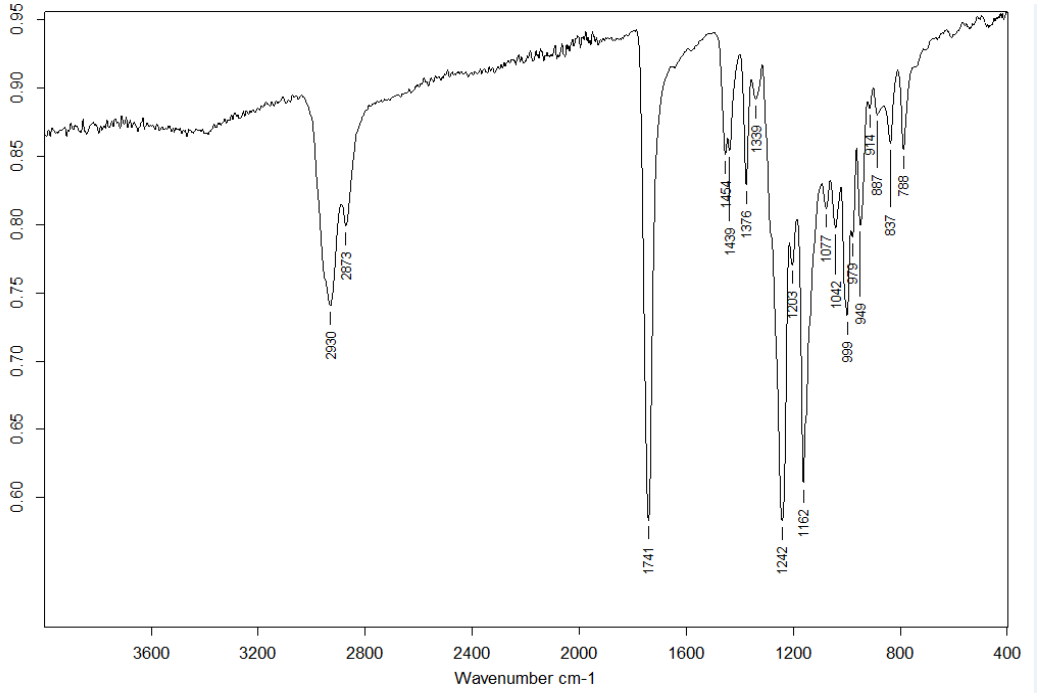
IR (neat, cm^{-1}): 1740 (C=O), 1646 (C=C).

Figure S40. IR spectrum of **CLP-100a**.



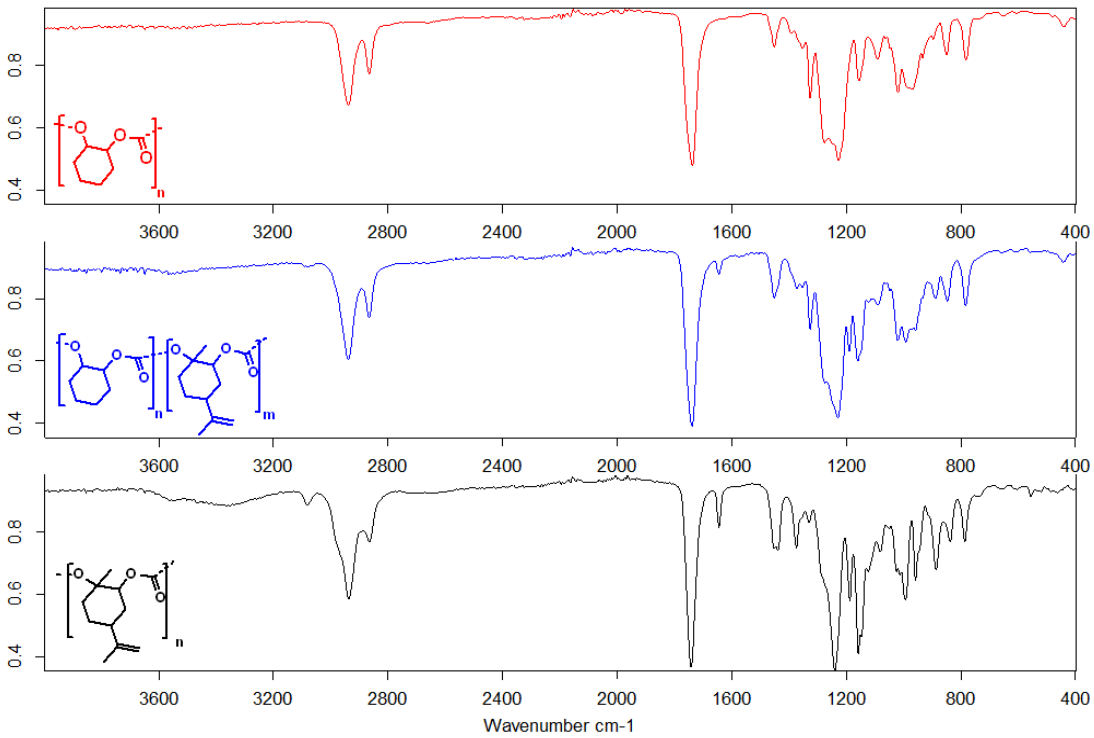
IR (neat, cm^{-1}): 1738 (C=O).

Figure S41. IR spectrum of **CLP-100b**.



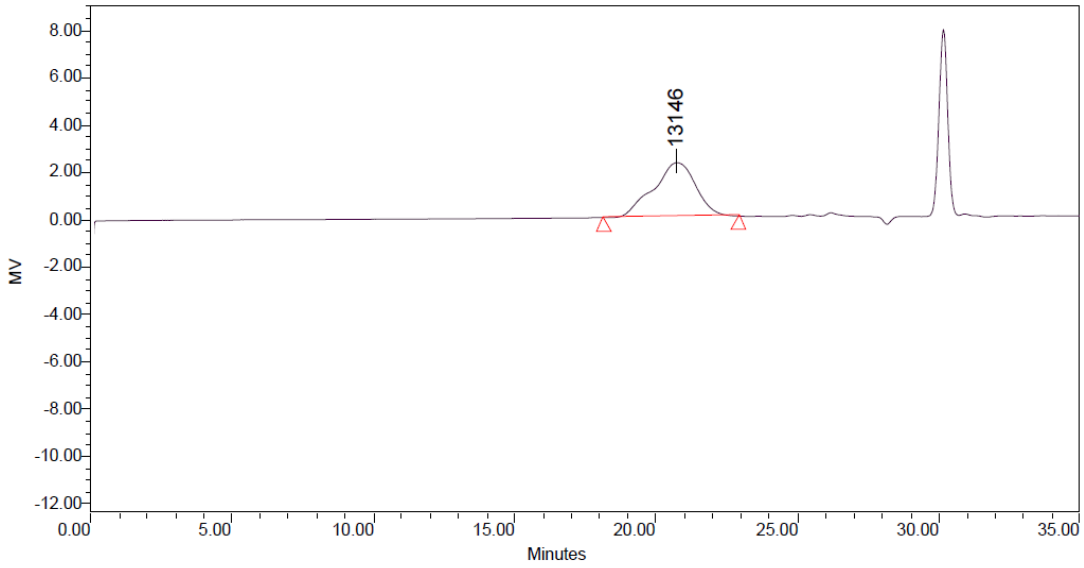
IR (neat, cm^{-1}): 1741 (C=O).

Figure S42. Comparative IR spectra for CHO/CO_2 copolymer (red trace), $CHO/LO/CO_2$ terpolymer (blue trace) and LO/CO_2 copolymer (black trace).



GPC ANALYSIS OF POLYMERS:

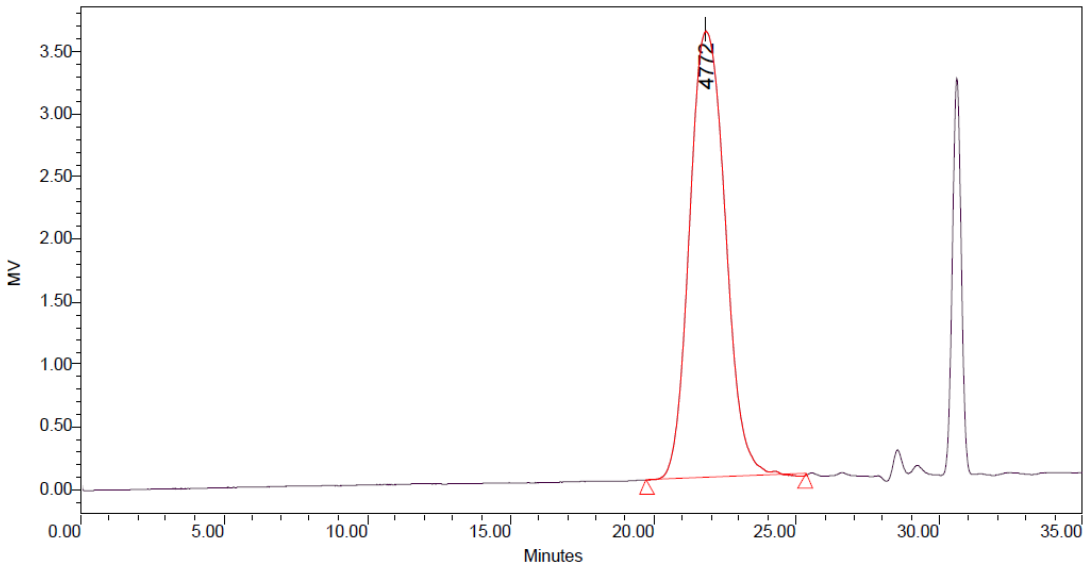
Figure S43. GPC trace of CHO/CO_2 copolymer, **P-0** (Table 1, entry 1).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		20.683	20.683	20.683	11936	17738	13146	25874	34799	1.458710

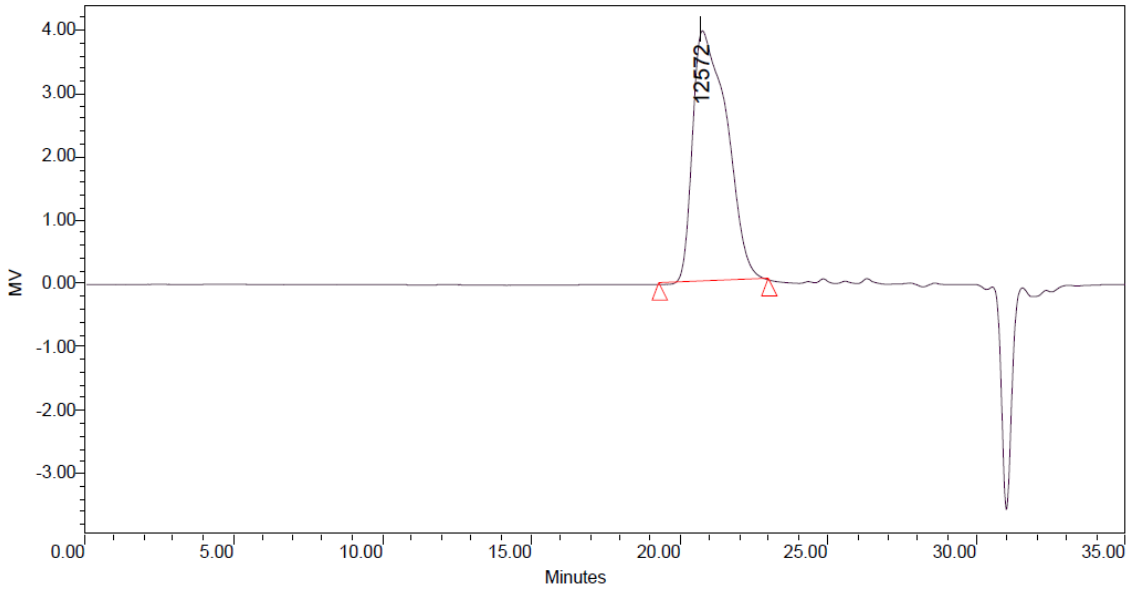
Figure S44. GPC trace of LO/CO_2 copolymer, **P-100** (Table 1, entry 6).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		21.800	21.800	21.800	3686	4954	4772	6281	7704	1.267782

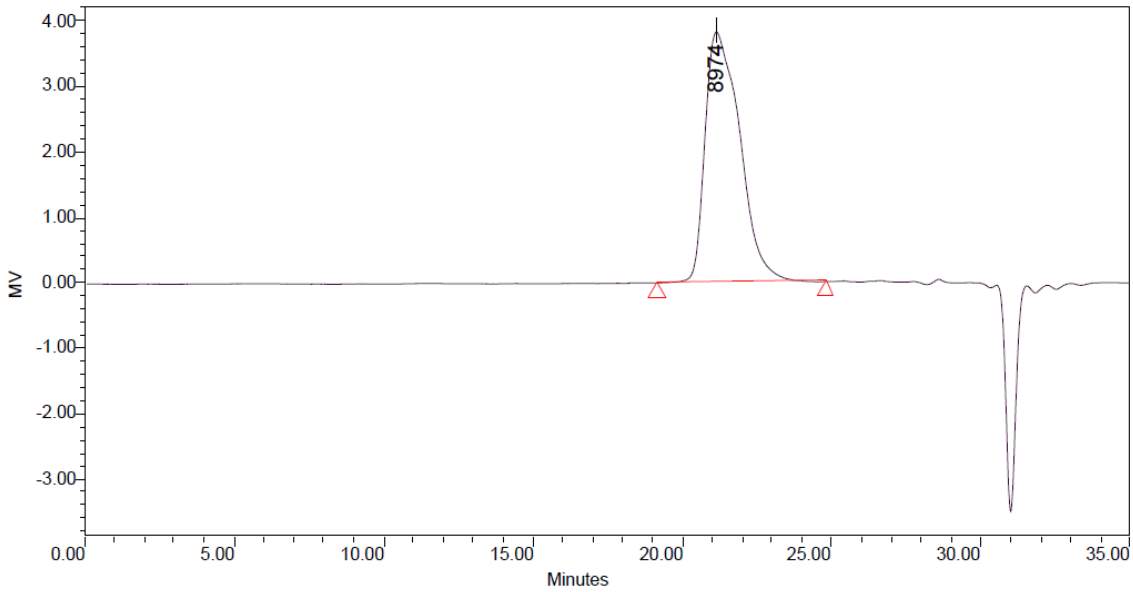
Figure S45. GPC trace of **T-10** (Table 1, entry 2).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		20.733	20.733	20.733	8219	10163	12572	12030	13675	1.183696

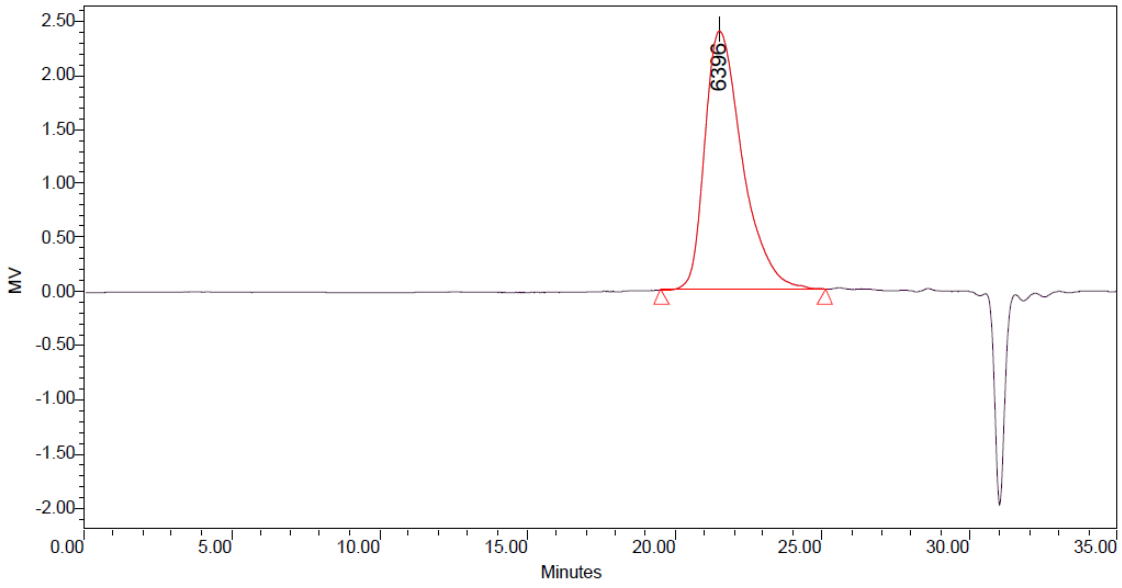
Figure S46. GPC trace of **T-20** (Table 1, entry 3).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		21.108	21.108	21.108	5815	7622	8974	9274	10945	1.216660

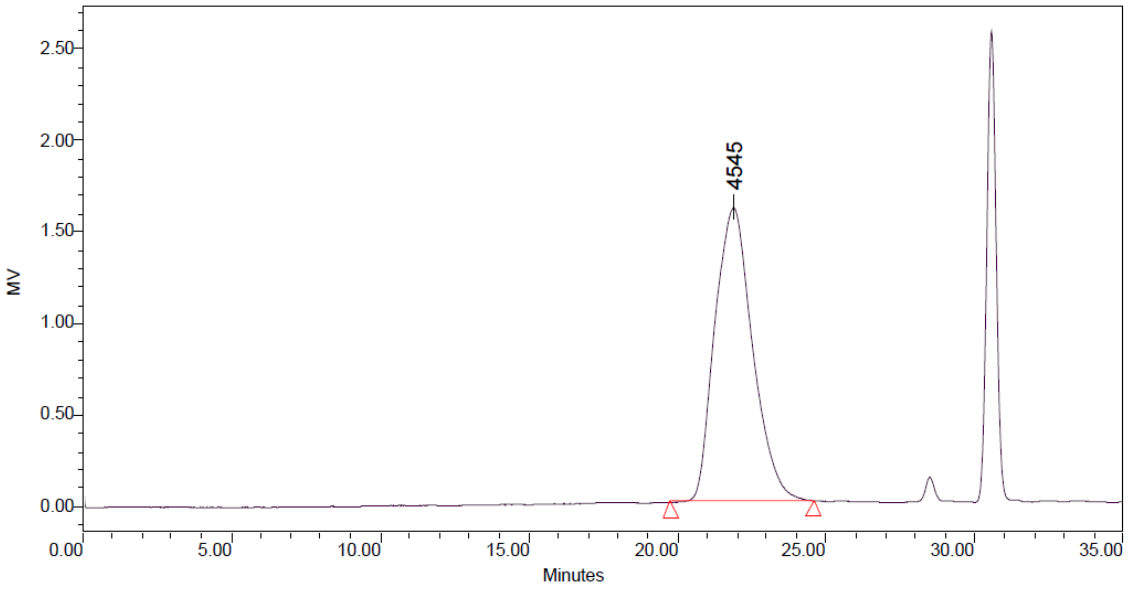
Figure S47. GPC trace of **T-30** (Table 1, entry 4).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		21.481	21.481	21.481	3955	5868	6396	7535	9109	1.284154

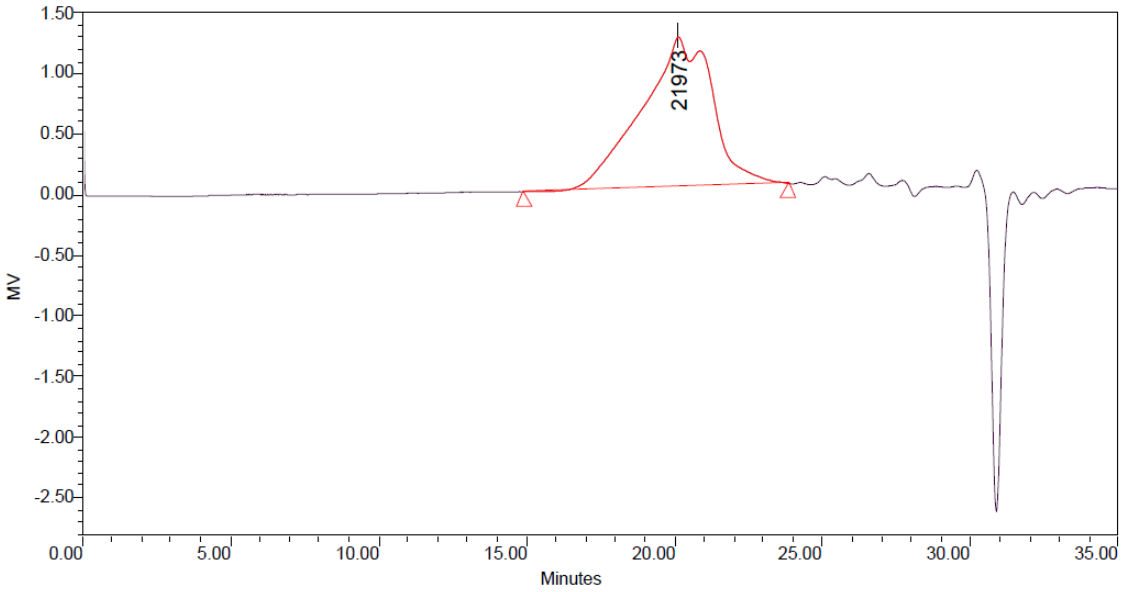
Figure S48. GPC trace of **T-40** (Table 1, entry 5).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		21.853	21.853	21.853	3581	4935	4545	6308	7673	1.278144

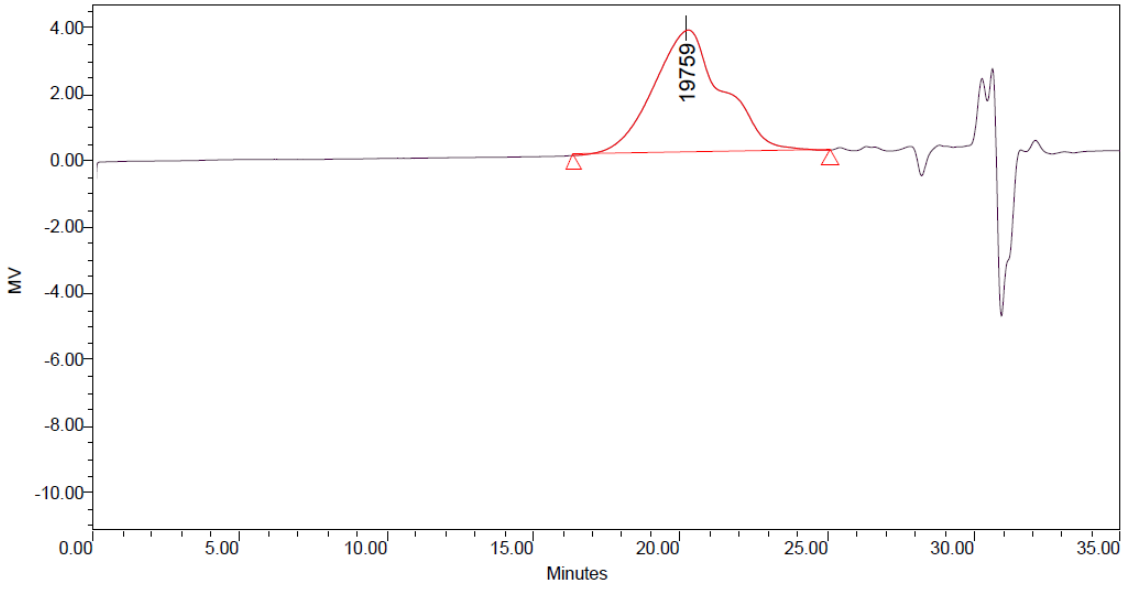
Figure S49. GPC trace of **CLP-10** (Table 3, entry 1).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		20.103	20.103	20.103	14626	42955	21973	108379	187748	2.523048

Figure S50. GPC trace of **CLP-100b** (Table 3, entry 7).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		20.224	20.224	20.224	9509	29963	19759	69508	127187	2.319780

MALDI-TOF MASS ANALYSIS OF POLYMERS:

MALDI-TOF-MS. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI) were performed by the Research Support Group at ICIQ on a BRUKER Autoflex spectrometer using 1 mg of sample per 1 mL of CH_2Cl_2. For CHO and LO copolymer, dctb was used as a matrix (10 mg/mL THF) and CF_3COONa as additive (1 mg/mL THF). For the terpolymers, dctb was used as a matrix (40 mg/mL THF) and CF_3COONa as additive (5 mg/mL THF).

Figure S51. MALDI-TOF mass spectrum of CHO copolymer, **P-0** (Table 1, Entry 1).

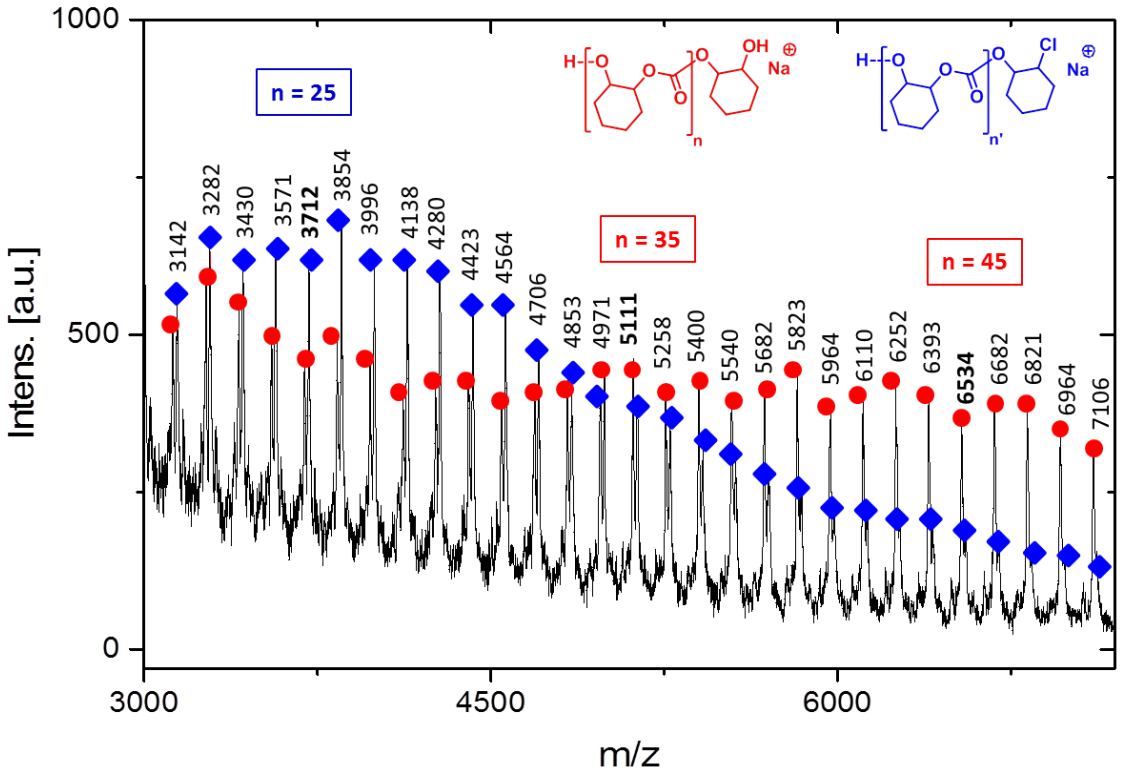
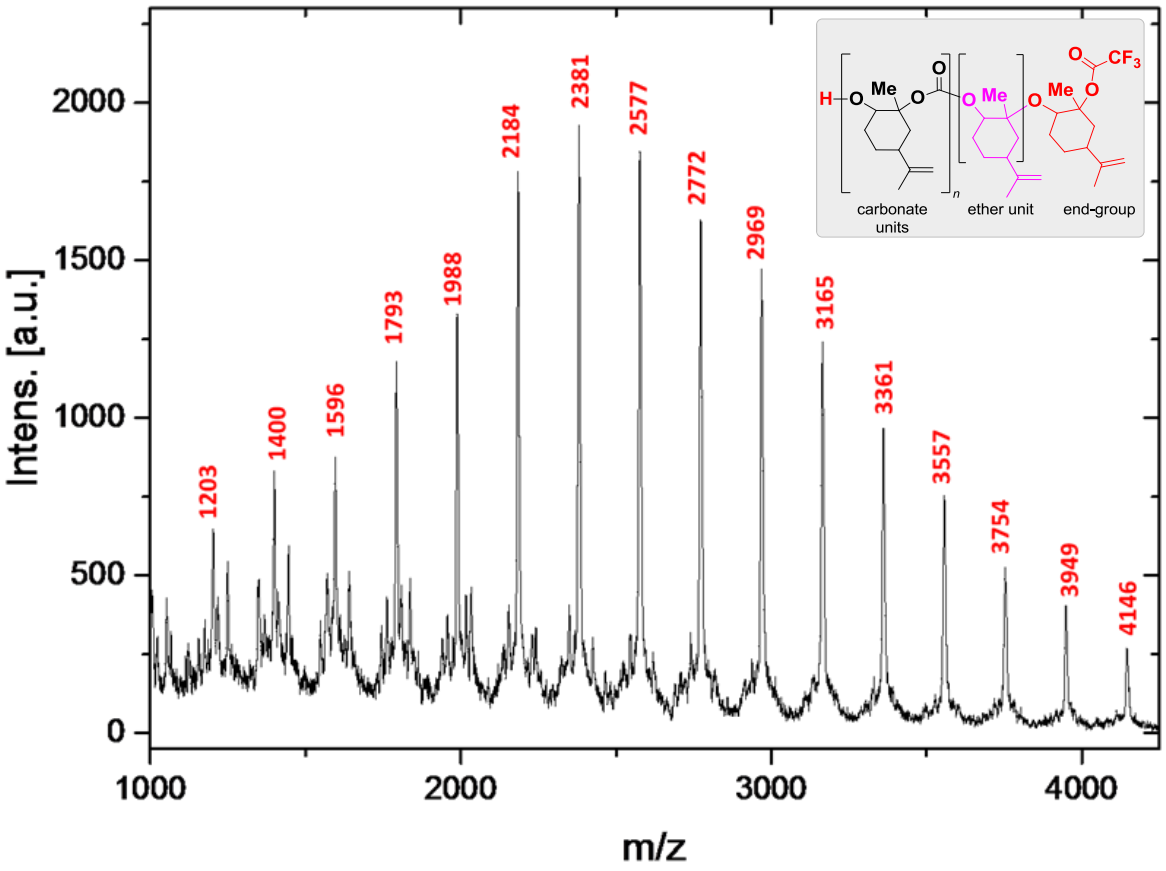


Figure S52. MALDI-TOF mass spectrum of LO copolymer P-**100** (Table 1, Entry 6).



In this MALDI-analysis, the assignment of the peaks in the major distribution was done on the basis of the incorporation of CF_3COO in the end-group of the polymer chain (Note: a $NaCF_3COO$ additive was added during the MALDI experiments).

For the copolymer having ***n* = 14** repeat units of LO/CO_2 (196.24), one ether linkage (152. 23) and an $OOCCF_3$ end-group (266.26) the calculated mass amounts to **3165.8** (noted: **3165**). The difference between all subsequent peaks equals a LO/CO_2 repeat unit (196).

Figure S53. MALDI-TOF mass spectrum of terpolymer **T-10** (Table 1, Entry 2).

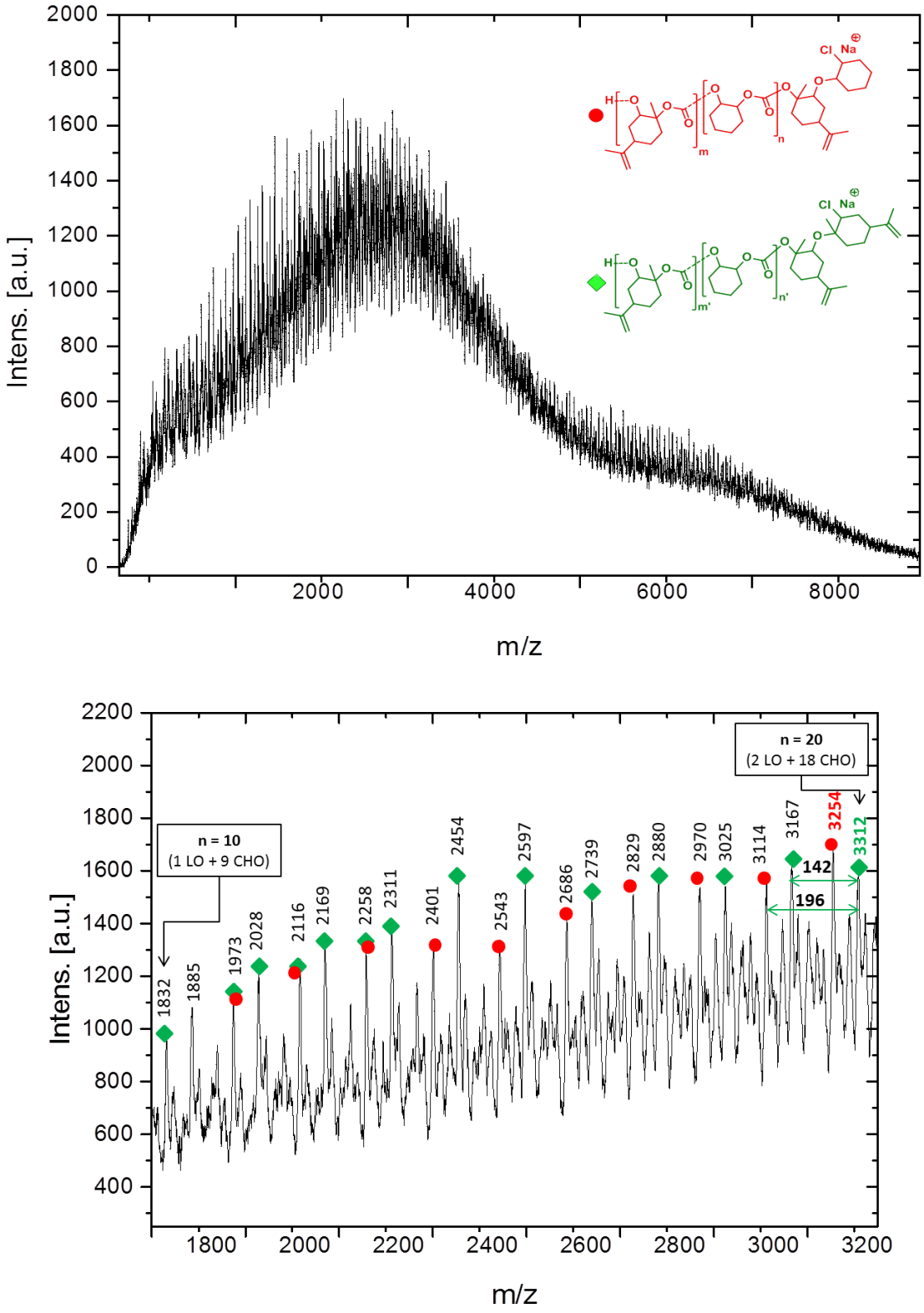


Figure S54. MALDI-TOF mass spectrum of terpolymer **T-20** (Table 1, Entry 3).

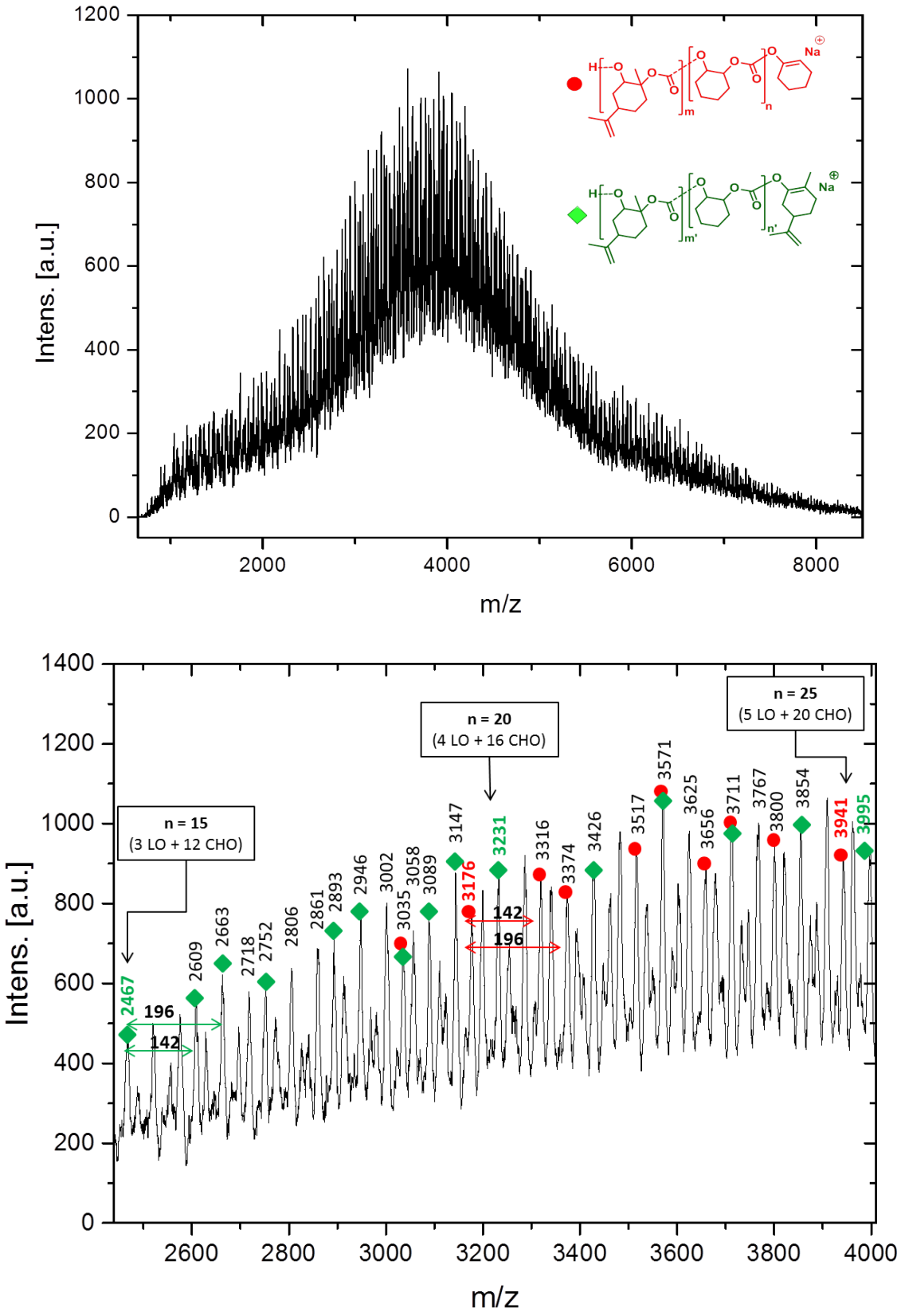


Figure S55. MALDI-TOF mass spectrum of terpolymer **T-30** (Table 1, Entry 4).

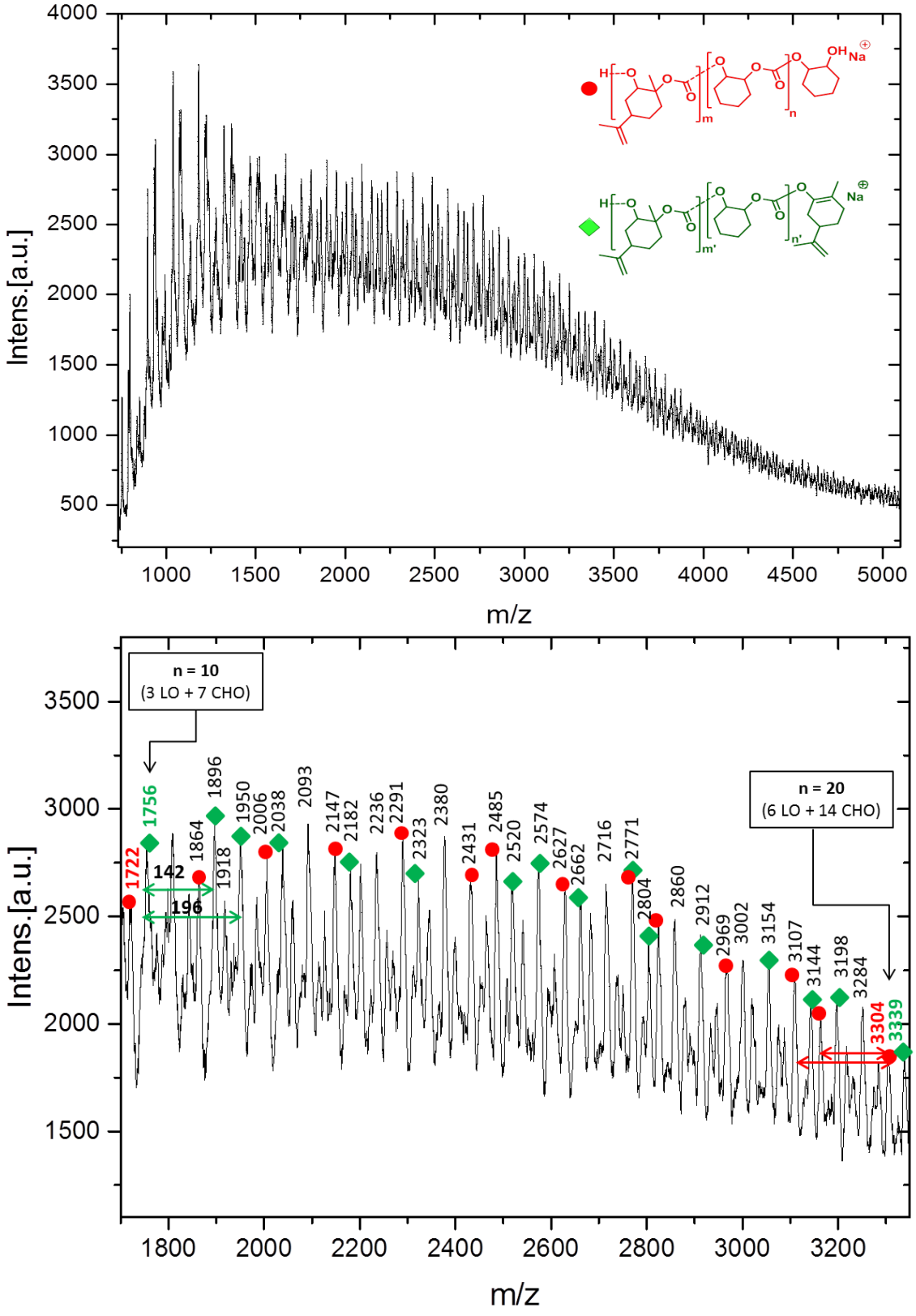
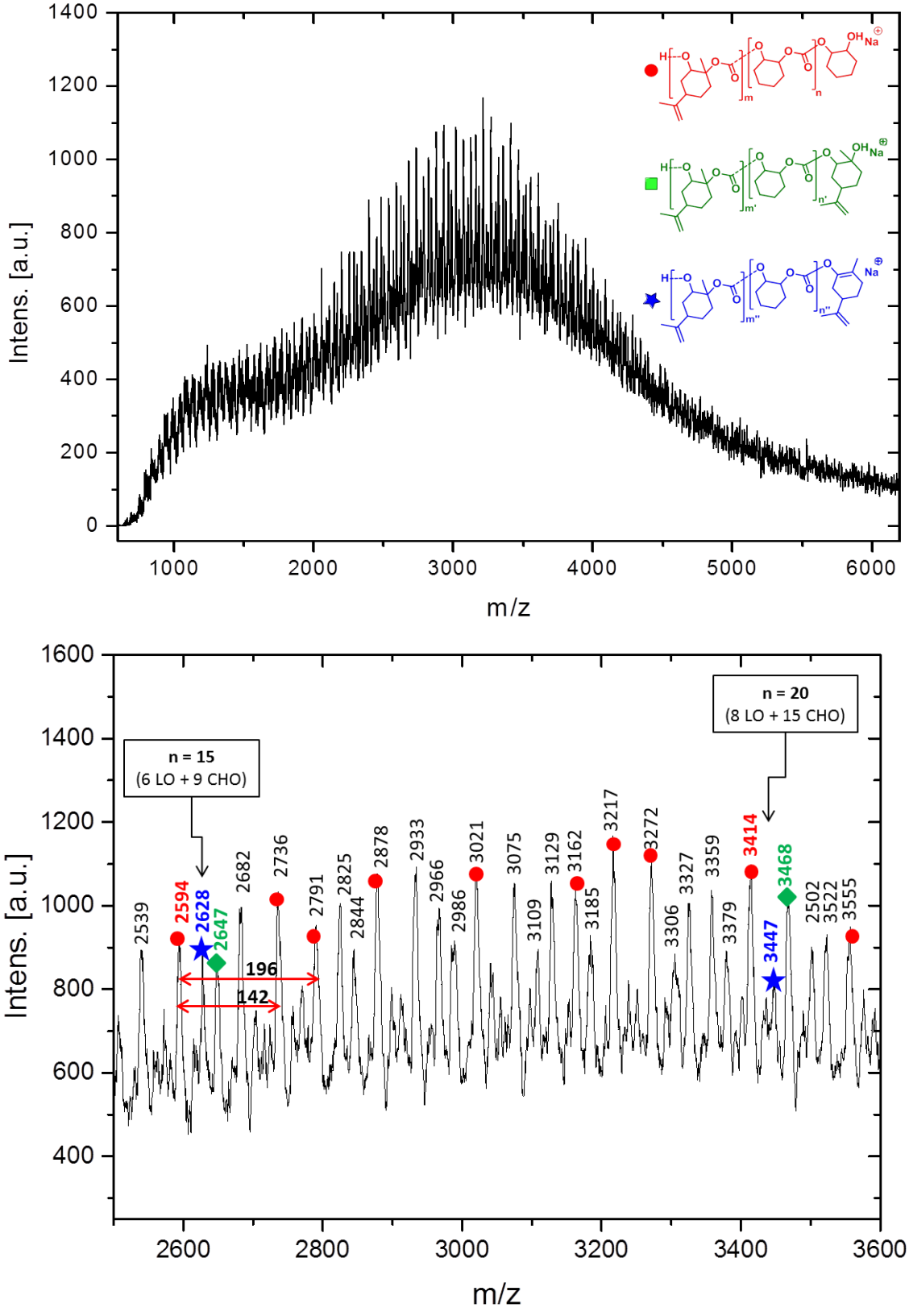


Figure S56. MALDI-TOF mass spectrum of terpolymer **T-40** (Table 1, Entry 5).



THERMAL (DSC & TGA) ANALYSIS OF POLYMERS:

Figure S57. DSC analysis of the terpolymer synthetized from 1 equiv. of CHO and 1 equiv. of *cis*-LO in the presence of 1.0 mol % of **Al^{Me}** and 0.5 mol % of PPNCl , at 45ºC and $p(CO_2)^0$ = 10 bar. Shown are the DSC traces after a first, second and third cycle, where several glass transition temperatures were observed.

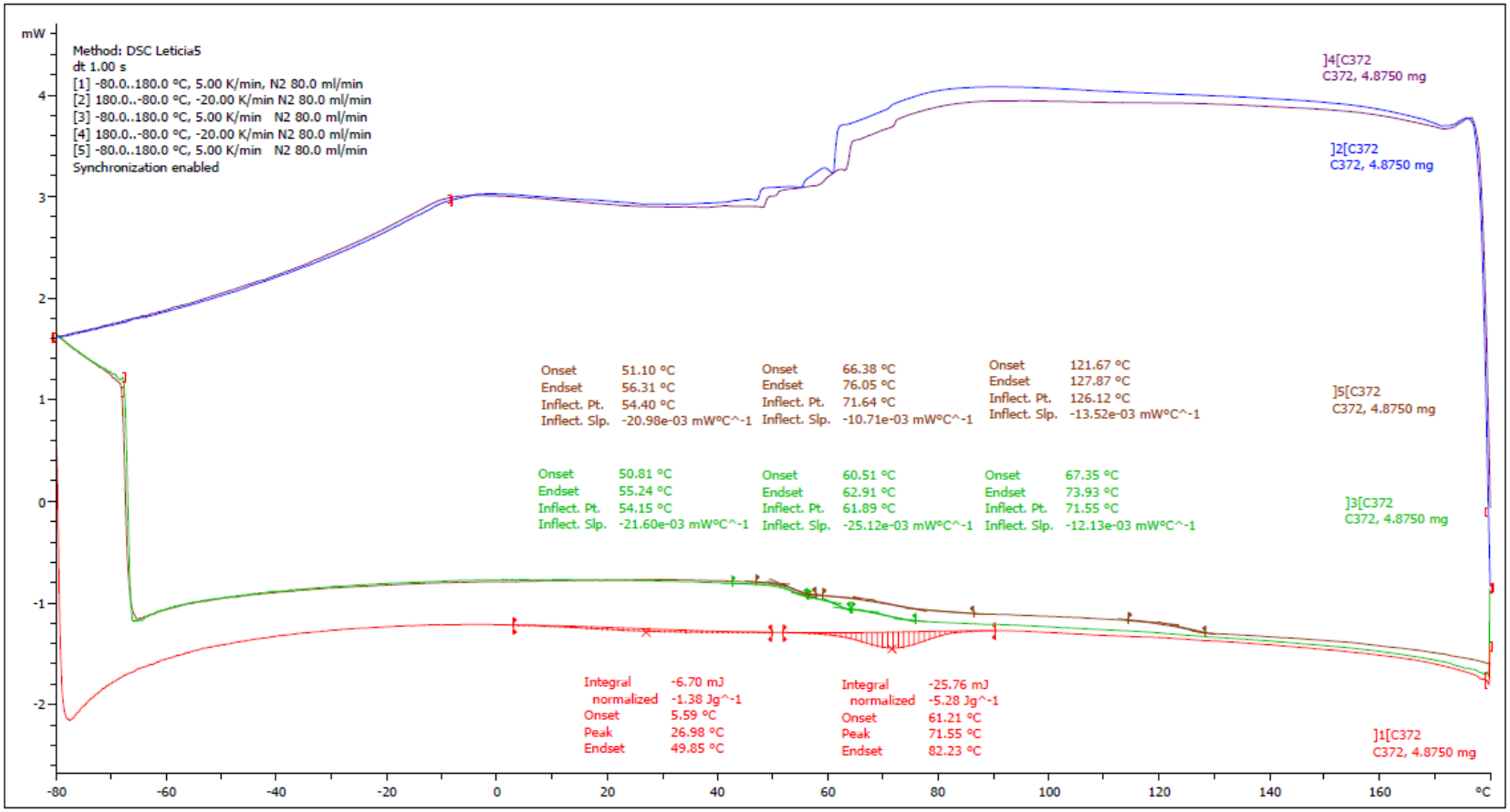


Figure S58. TGA of CHO/CO_2 copolymer, **P-0** (T_d = 248.64ºC at 10 % weight loss of polymer).

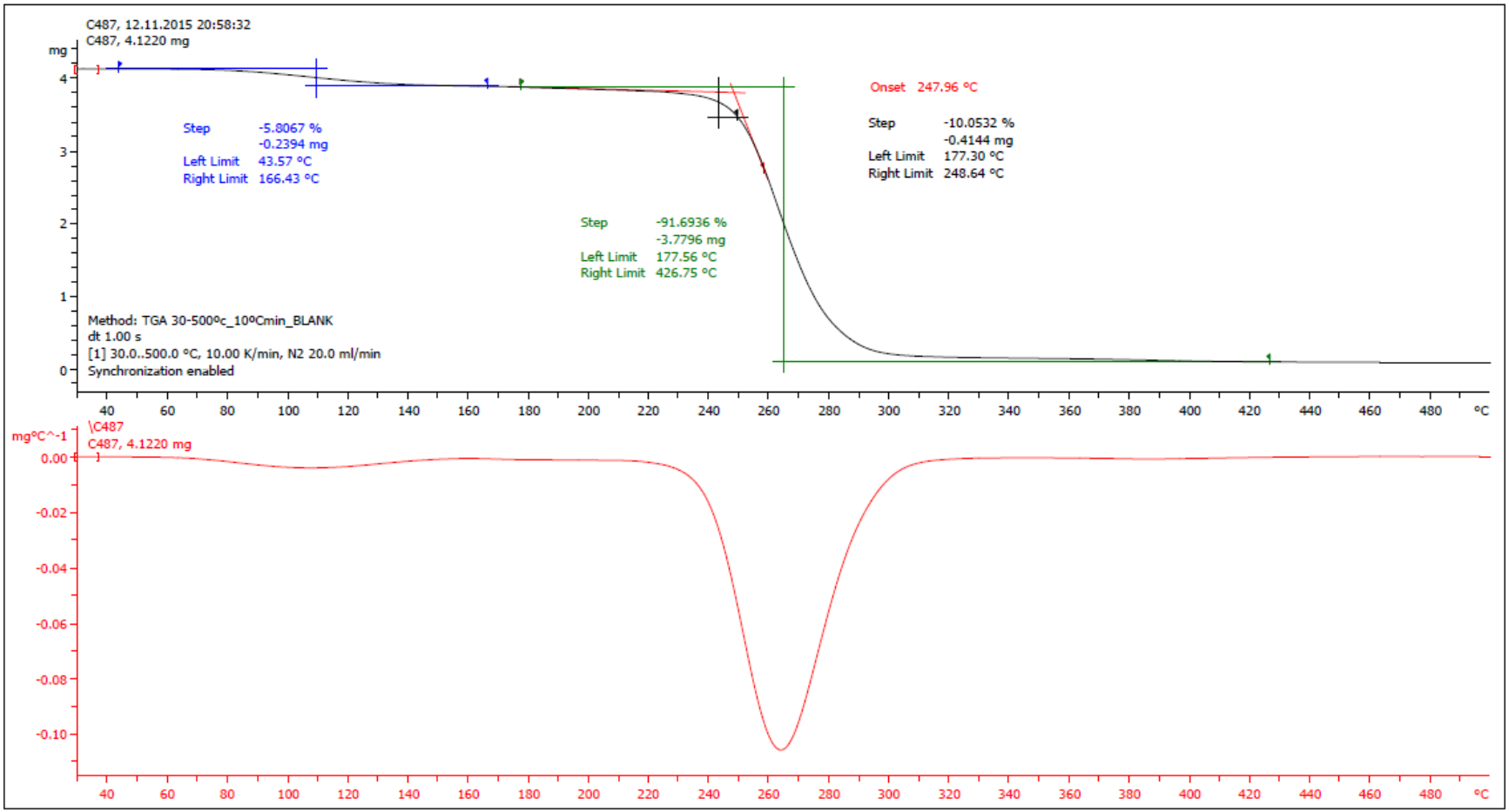


Figure S59. DSC analysis of the CHO/CO_2 copolymer, **P-0** (Table 1, entry 1). Shown are the DSC traces after a second and third cycle (T_g´s: 115.14 and 113.81ºC, respectively).

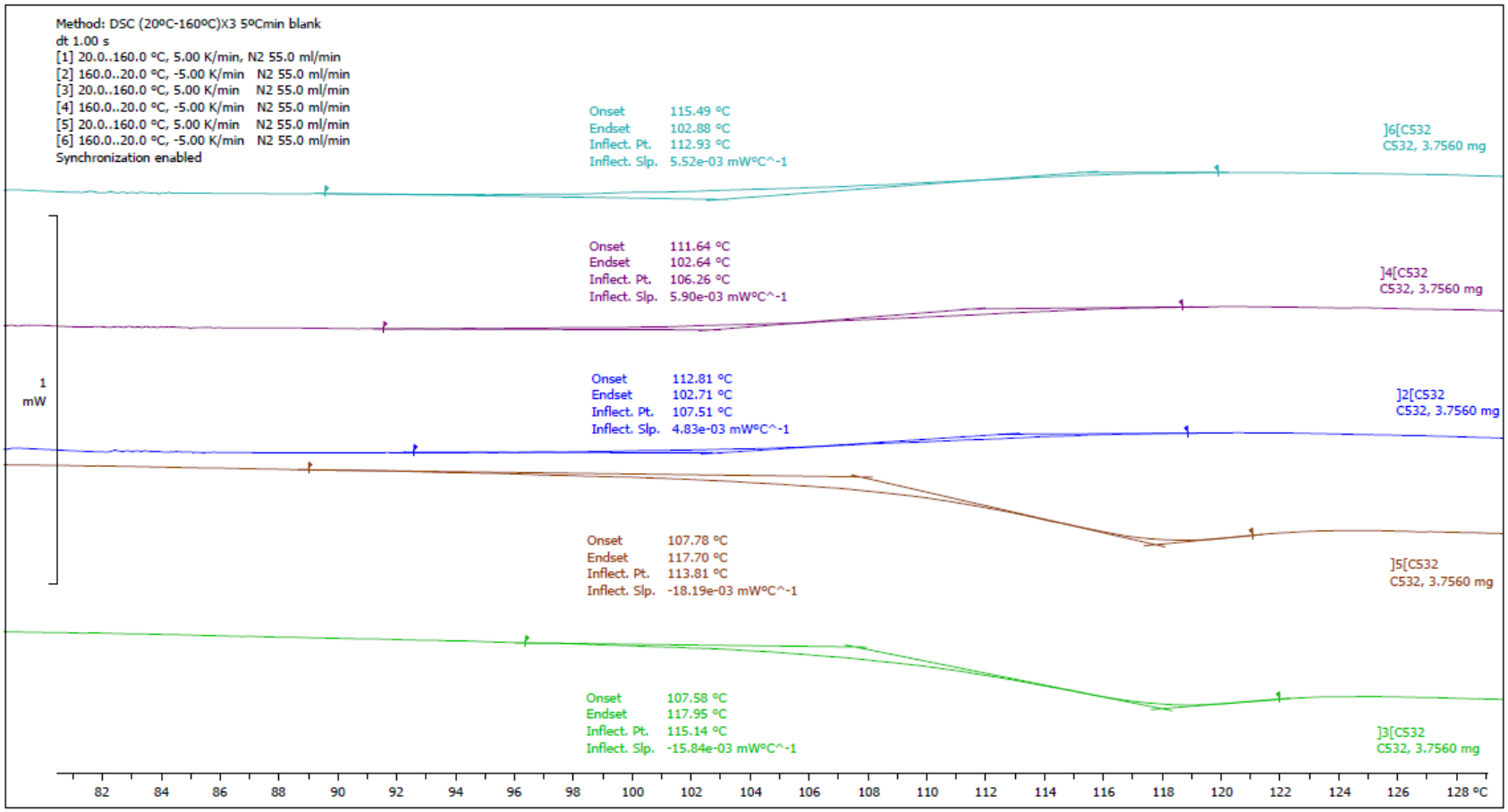


Figure S60. TGA of LO/CO_2 copolymer, **P-100** (T_d = 225.69ºC at 10 % weight loss of polymer).

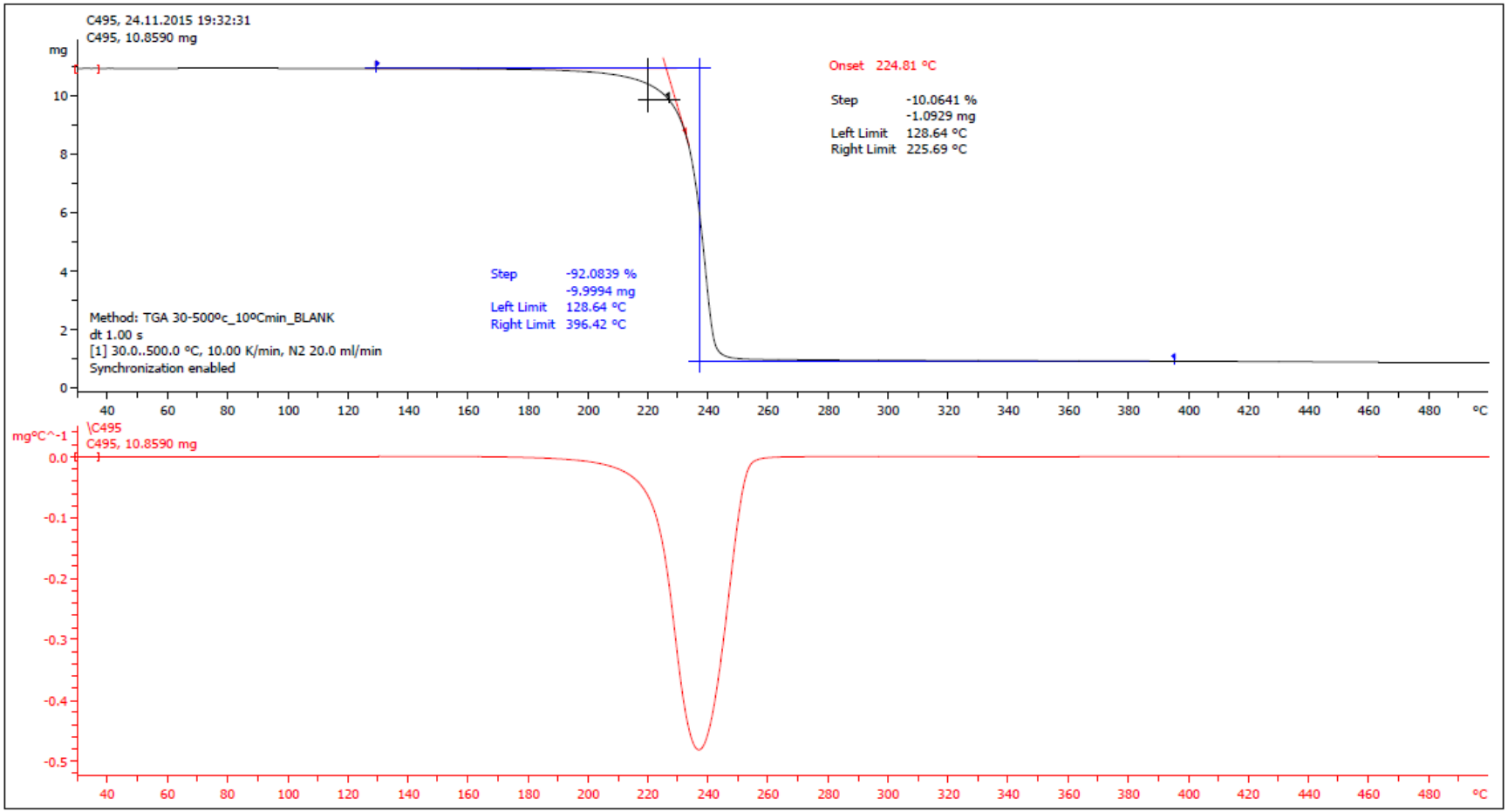


Figure S61. DSC analysis of the LO/CO_2 copolymer, **P-100** (Table 1, entry 6). Shown are the DSC traces after a second and third cycle (T_g´s: 72.04 and 71.79ºC, respectively).

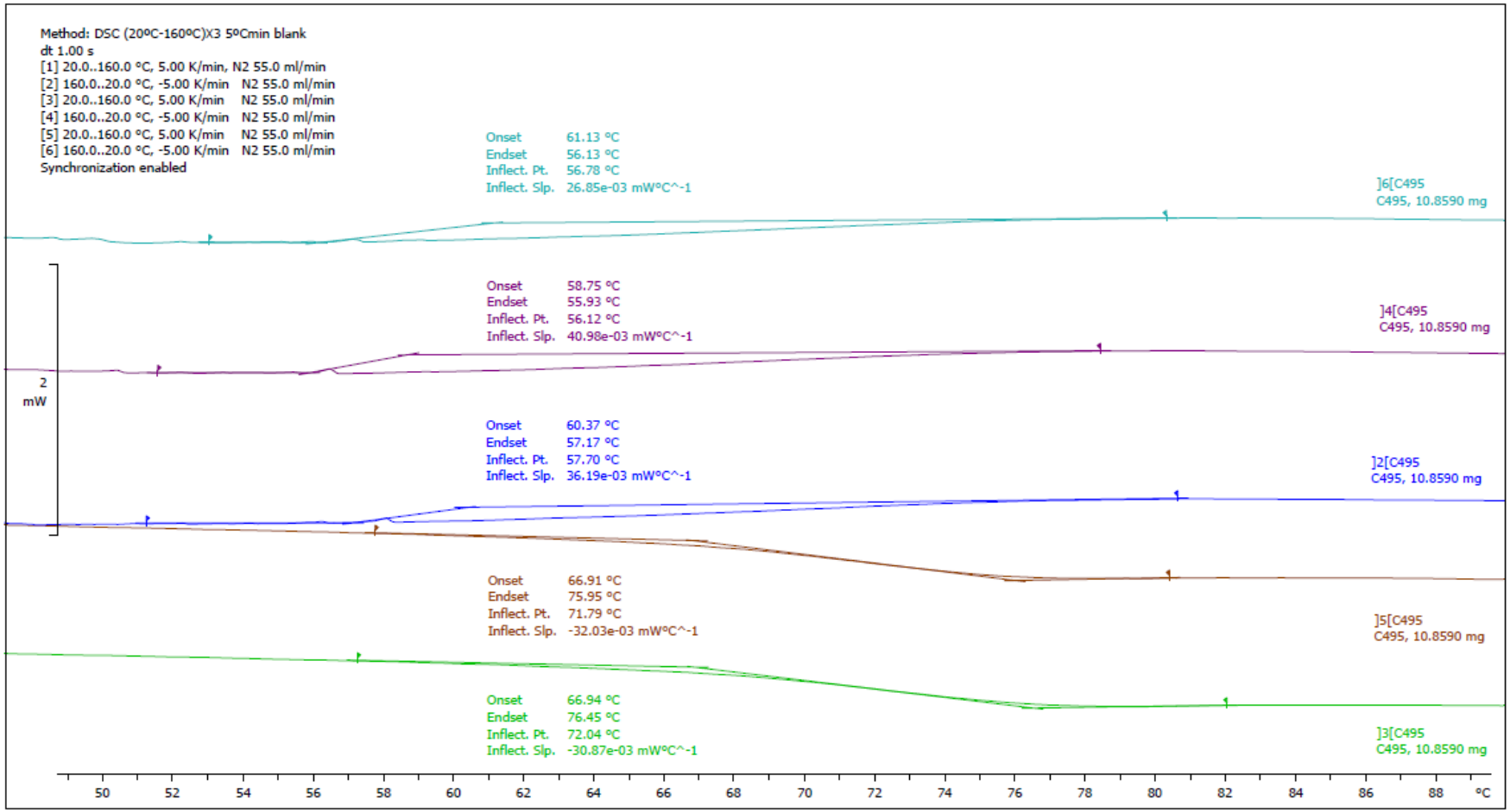


Figure S62. TGA of terpolymer **T-10** (T_d = 262.67ºC at 10 % weight loss of polymer).

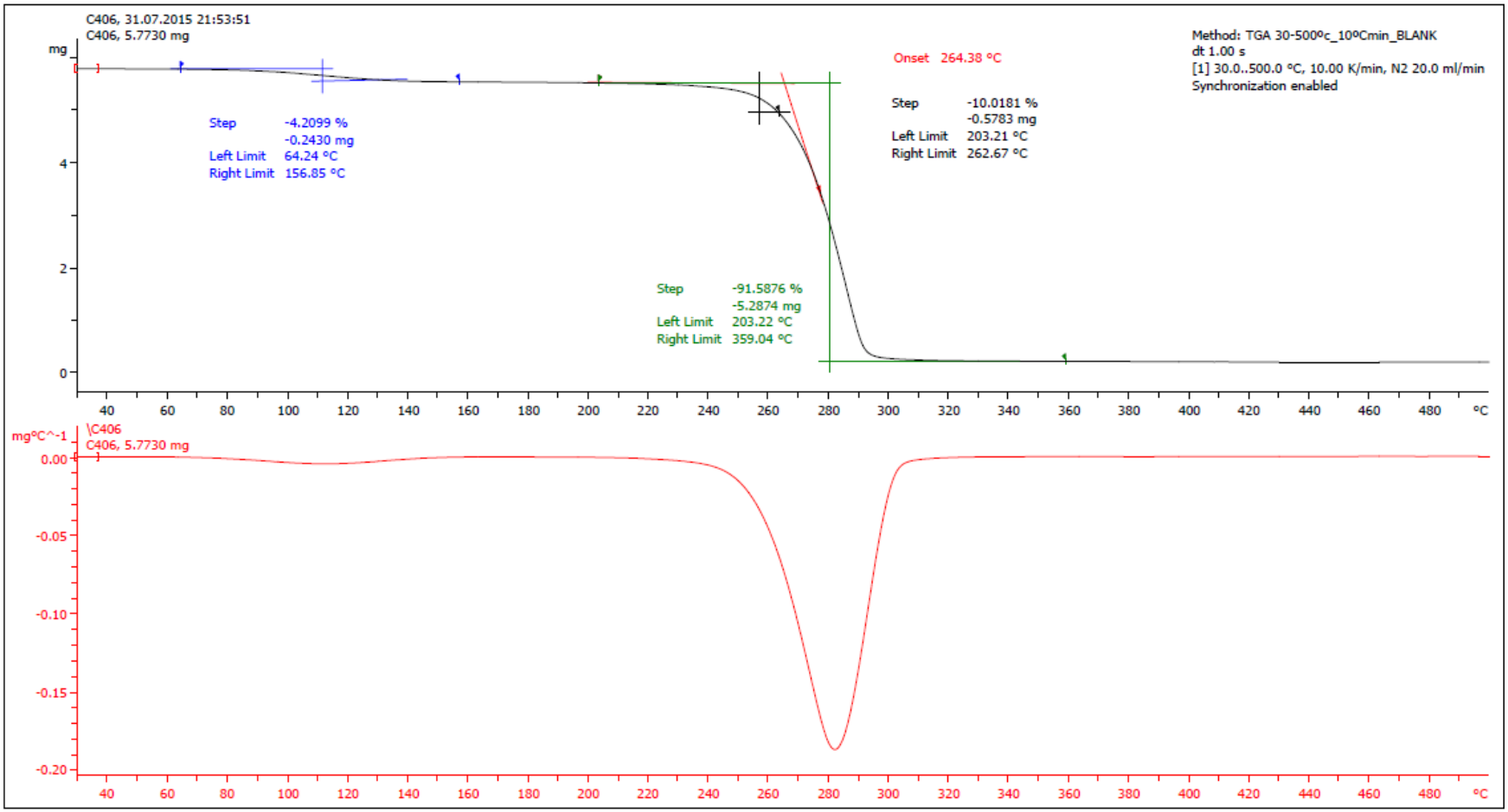


Figure S63. DSC analysis of the terpolymer **T-10** (Table 1, entry 2). Shown are the DSC traces after a second and third cycle (T_g´s: 111.54 and 110.95ºC, respectively).

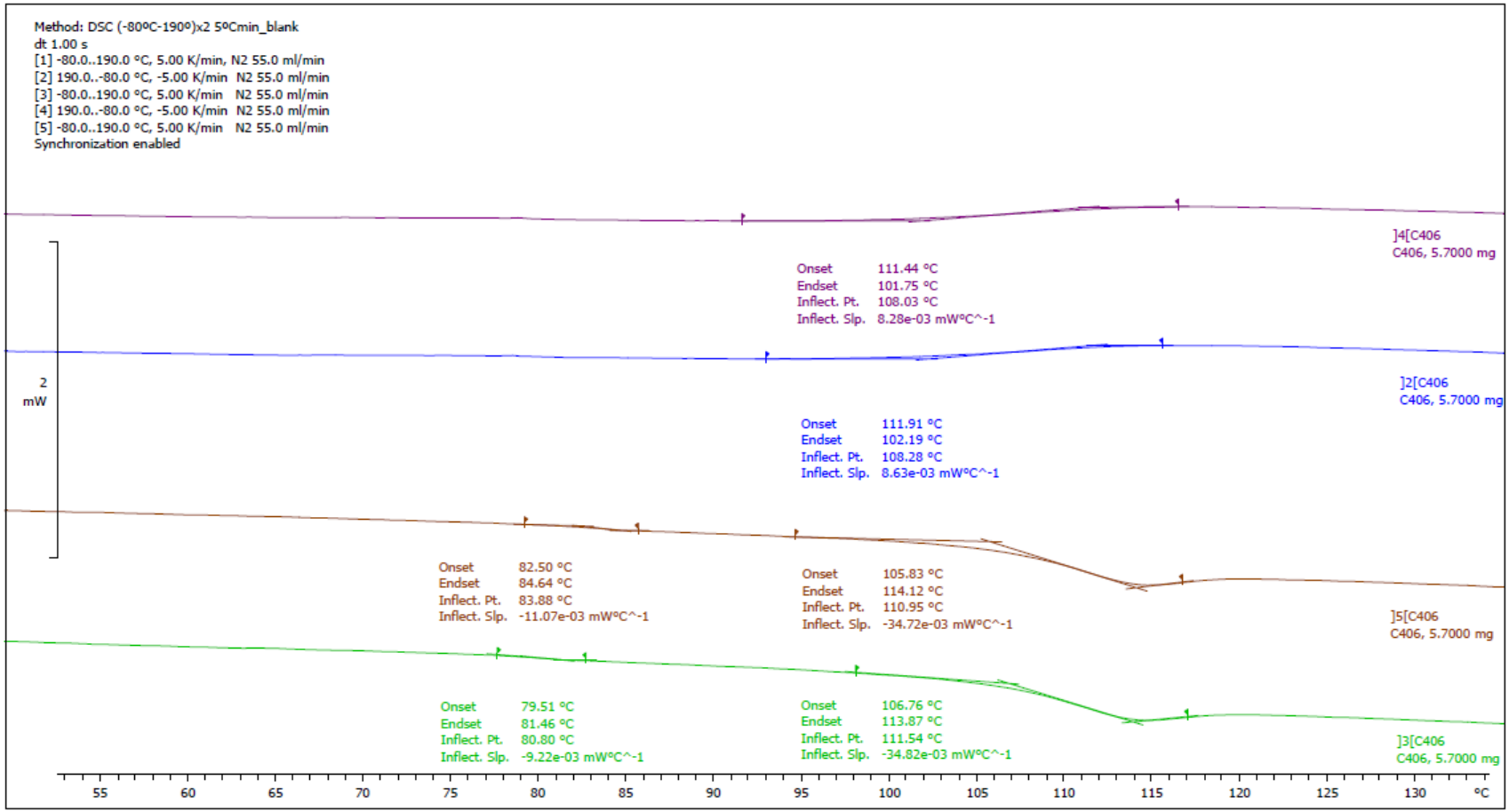


Figure S64. TGA of terpolymer **T-20** (T_d = 247.74ºC at 10 % weight loss of polymer).

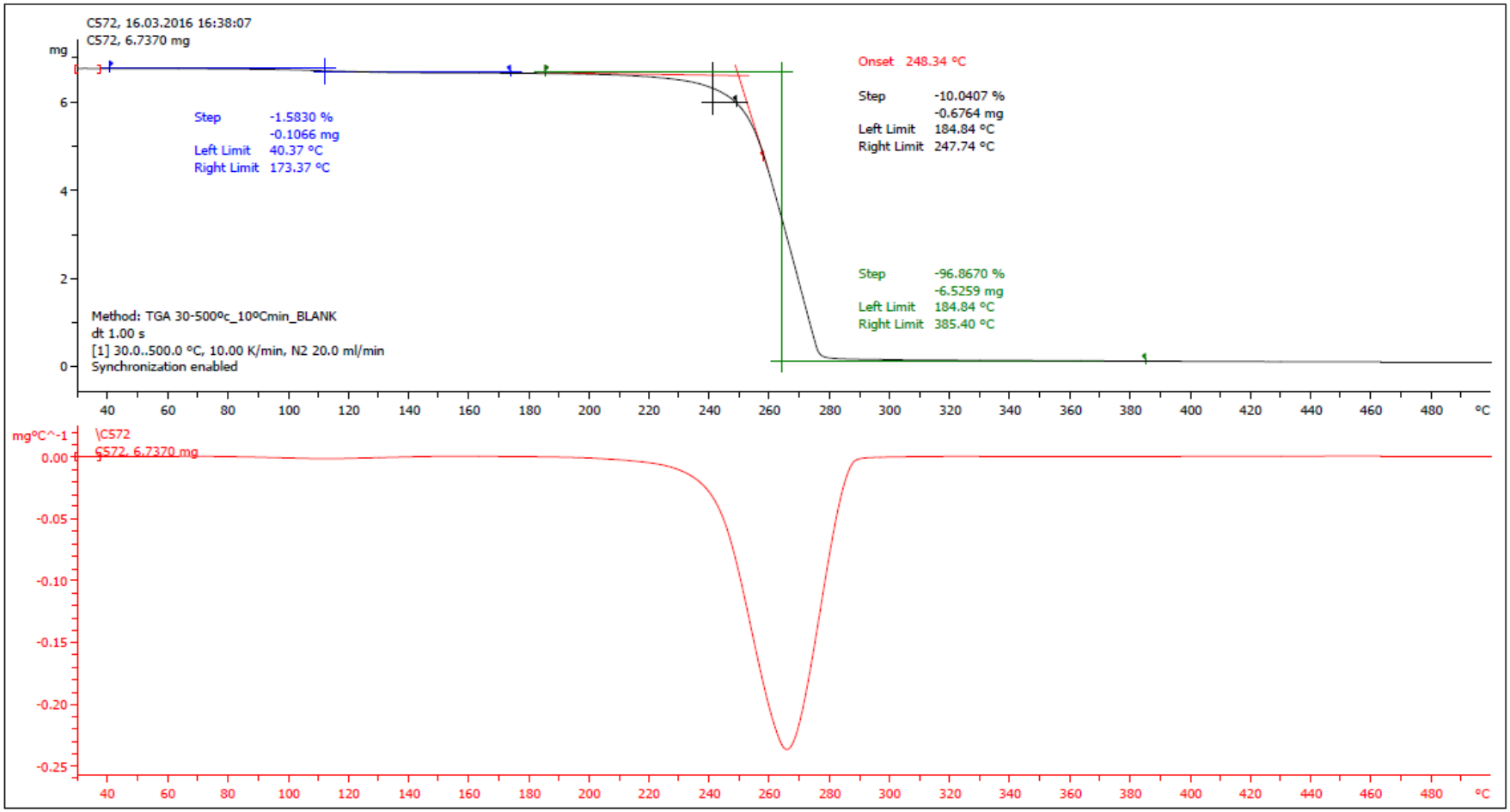


Figure S65. DSC analysis of the terpolymer **T-20** (Table 1, entry 3). Shown are the DSC traces after a second and third cycle (T_g´s: 108.86 and 108.78ºC, respectively).

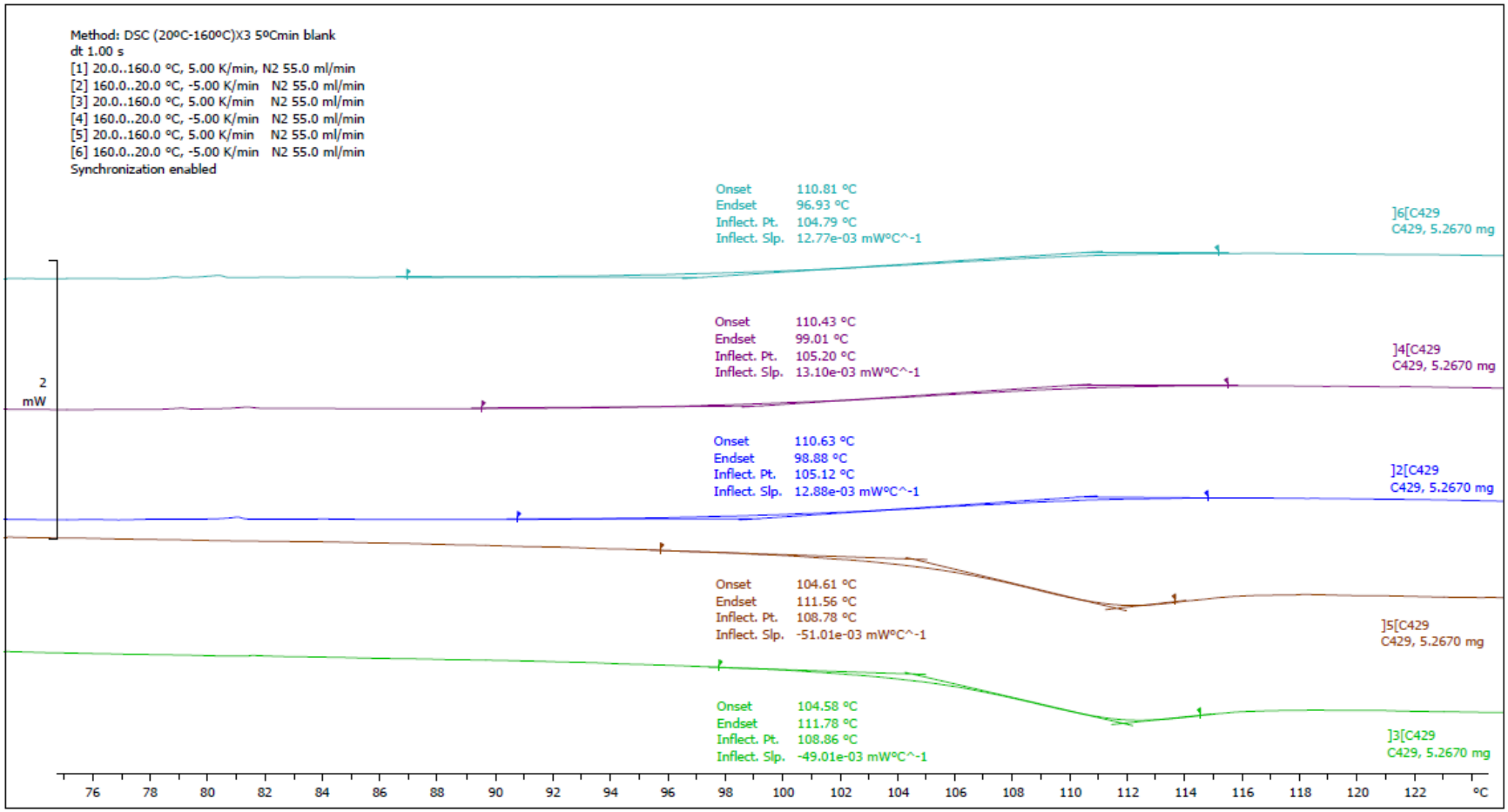


Figure S66. TGA of terpolymer **T-30** (T_d = 210.09ºC at 10 % weight loss of polymer).

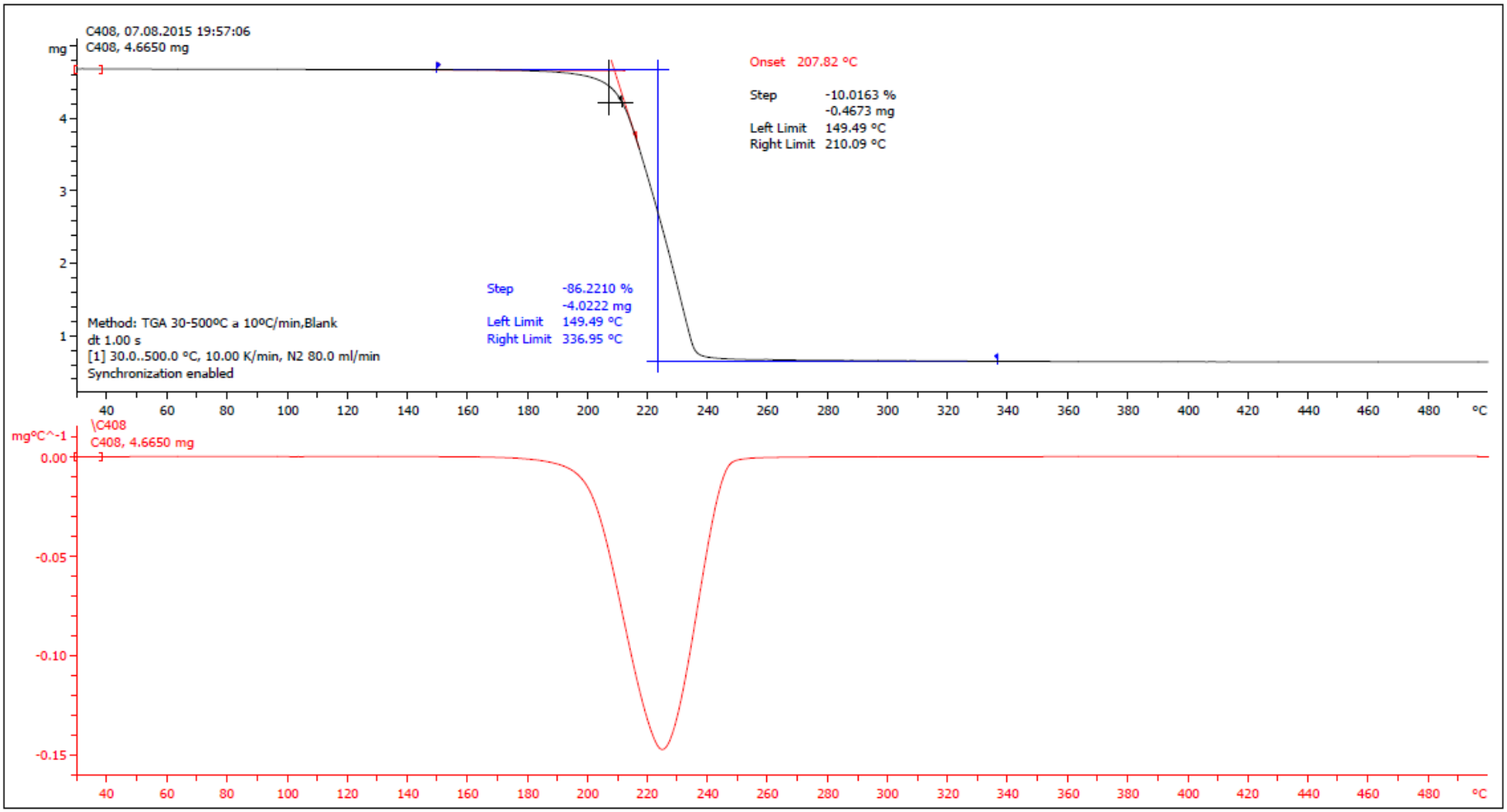


Figure S67. DSC analysis of the terpolymer **T-30** (Table 1, entry 4). Shown are the DSC traces after a second and third cycle (T_g´s: 94.64 and 95.56ºC, respectively).

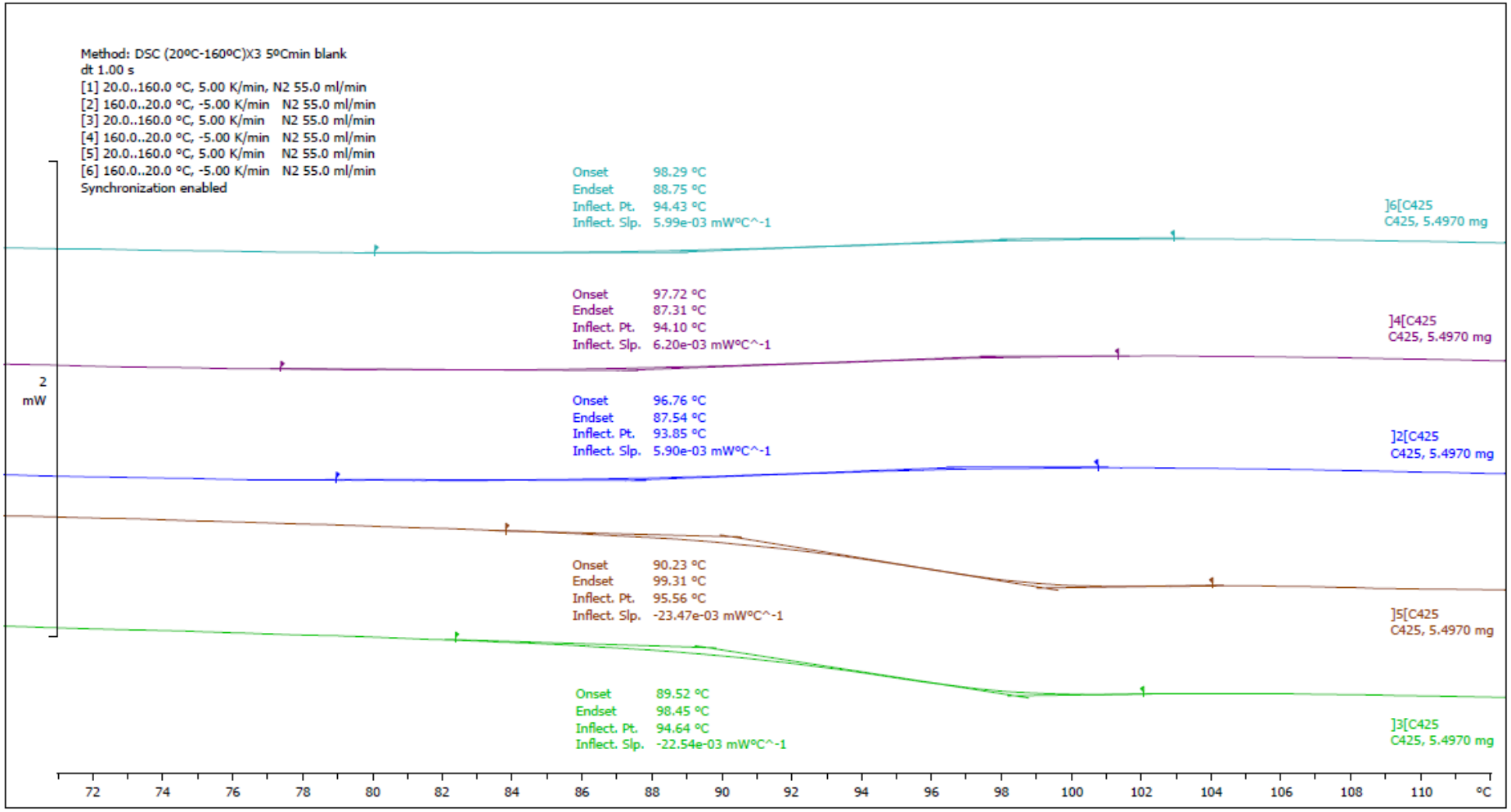


Figure S68. TGA of terpolymer **T-40** (T_d = 227.90ºC at 10 % weight loss of polymer).

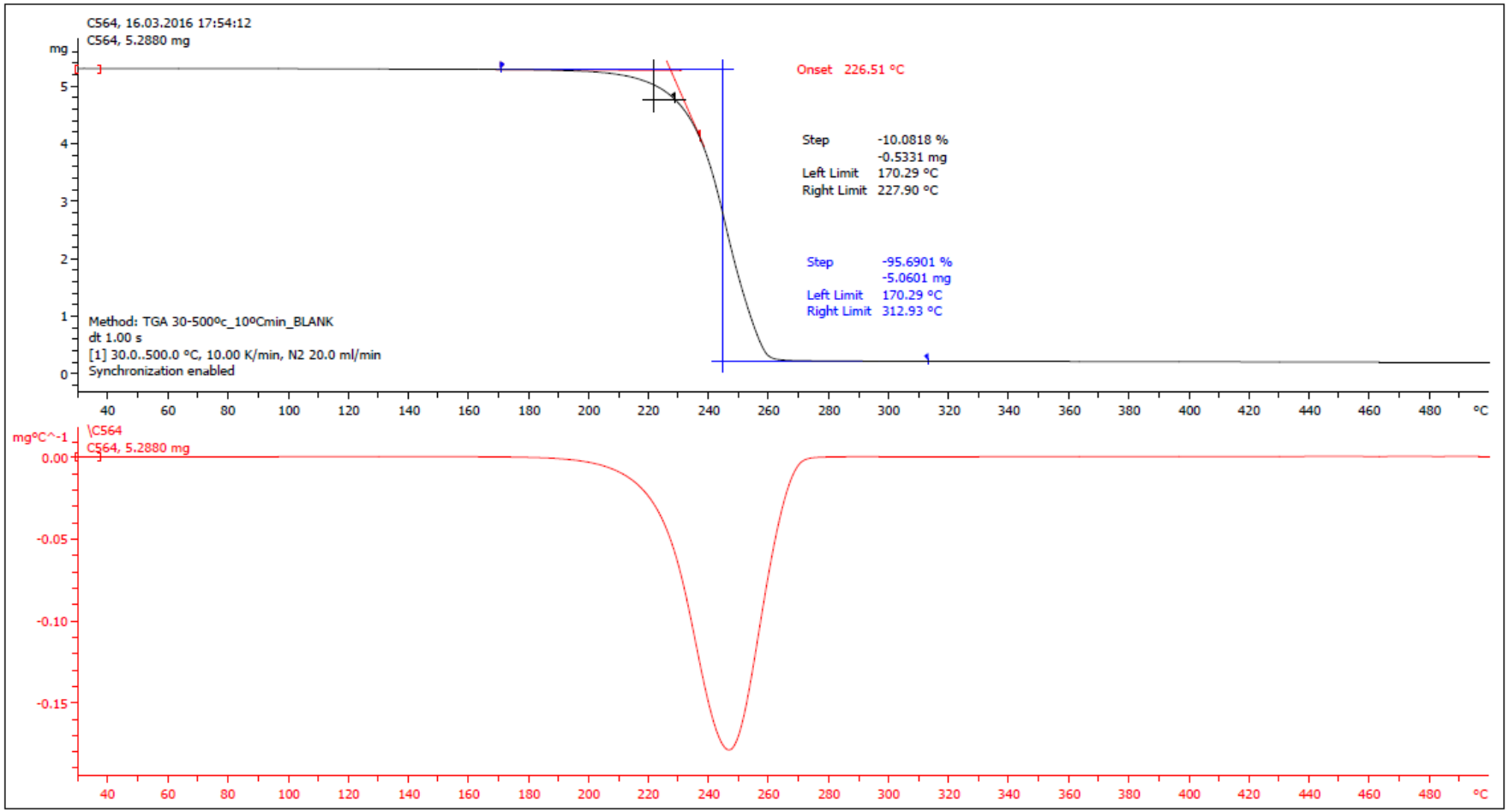


Figure S69. DSC analysis of the terpolymer **T-40** (Table 1, entry 5). Shown are the DSC traces after a second and third cycle (*Tg´s*: 85.33 and 83.25ºC, respectively).

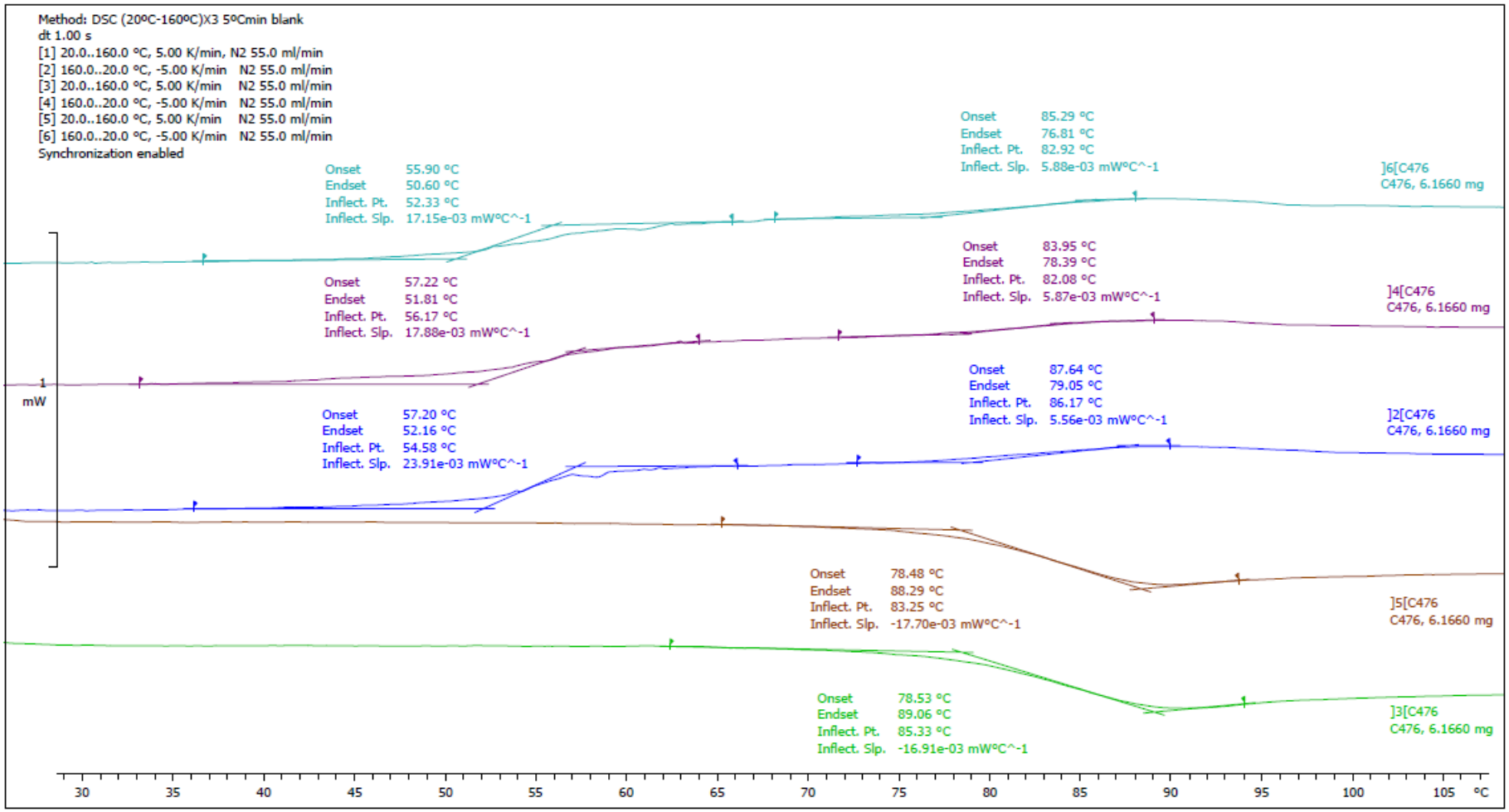


Figure S70. TGA of **CLP-10** (T_d = 282.18ºC at 10 % weight loss of polymer).

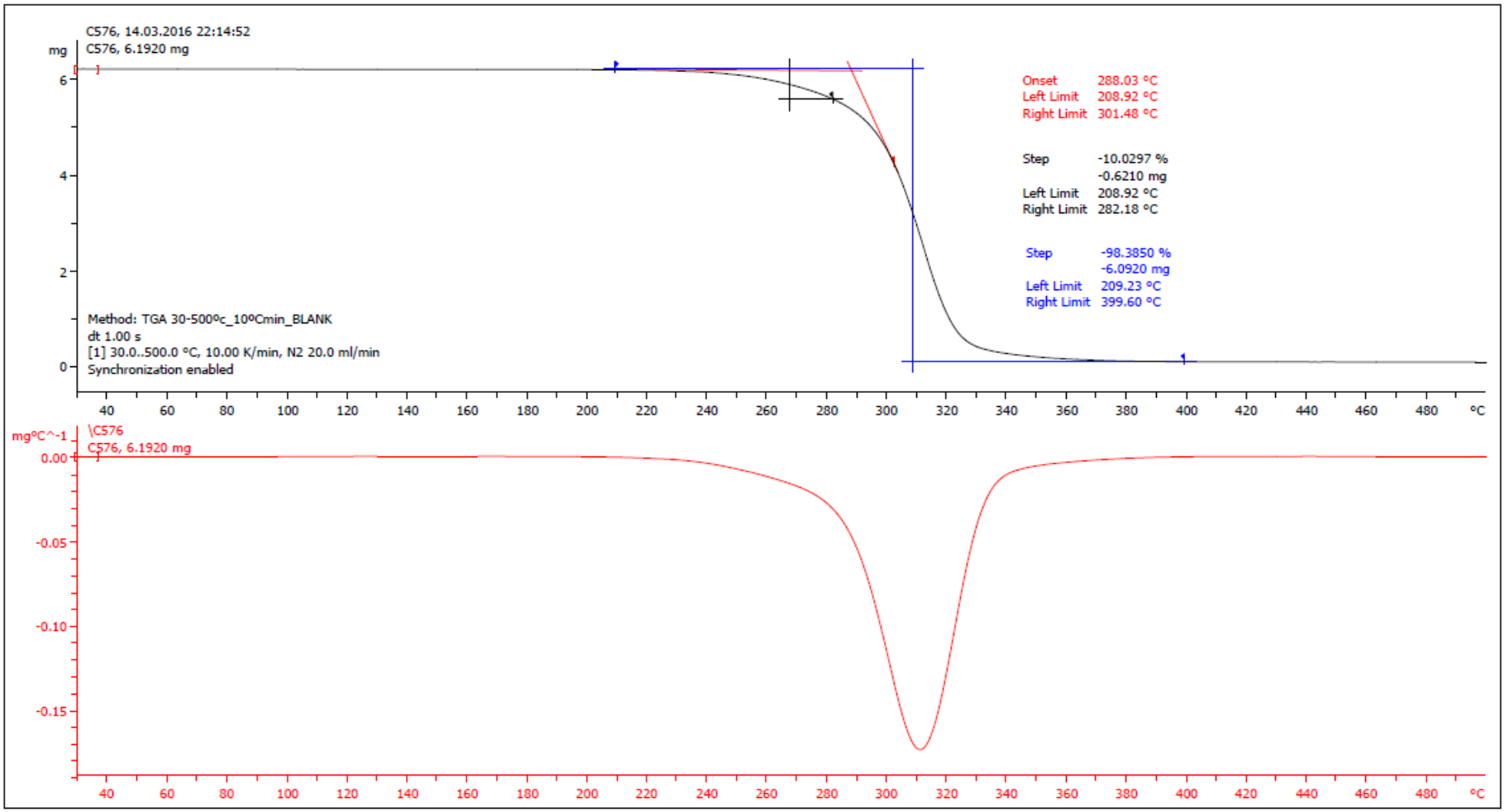


Figure S71. DSC analysis of the **CLP-10** (Table 3, entry 1). Shown are the DSC traces after a first, second, third and fourth cycle (T_g´s: 119.9, 117.07, 116.91 and 116.91ºC, respectively).

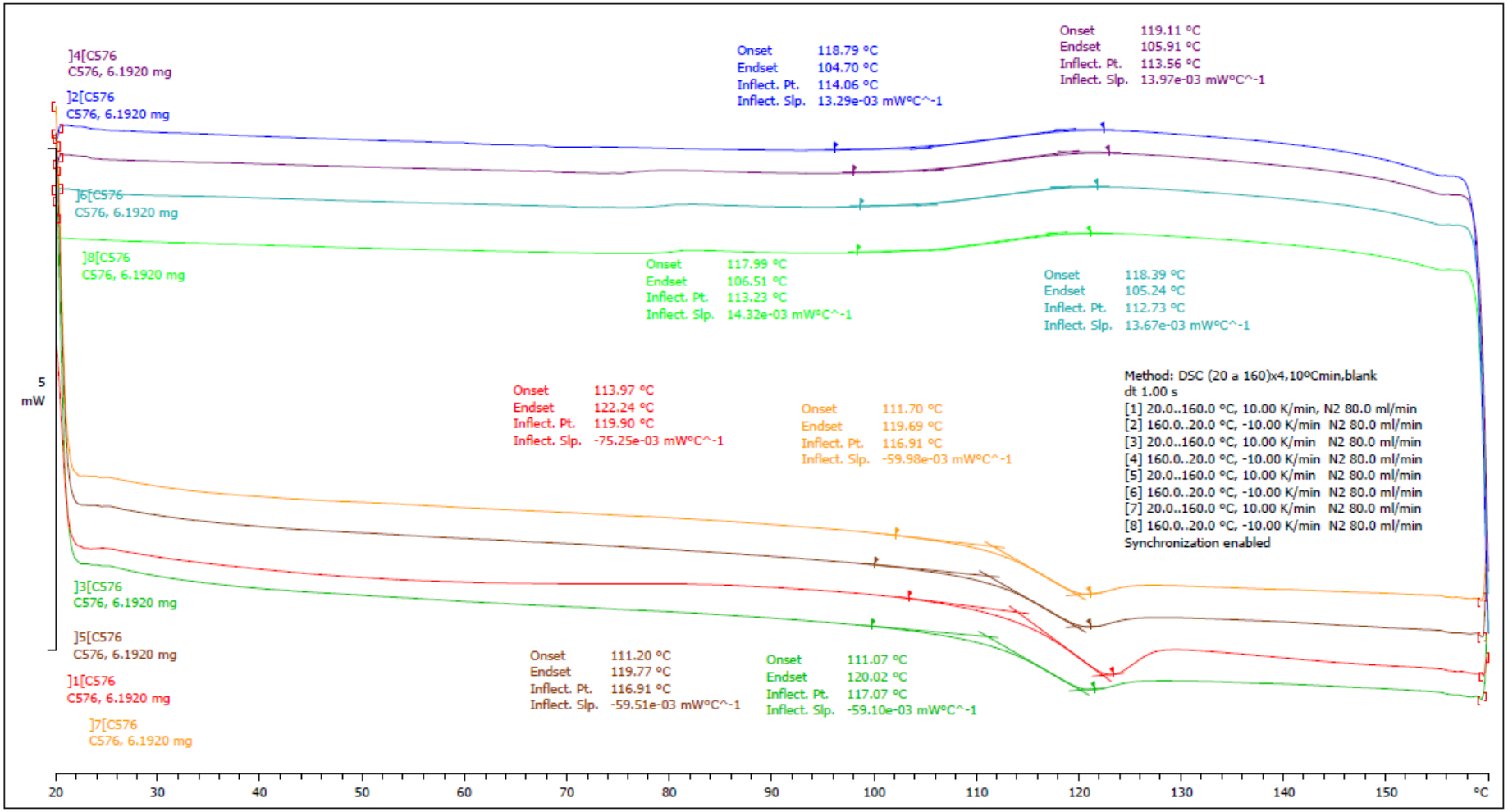


Figure S72. TGA of **CLP-20** (T_d = 279.35ºC at 10 % weight loss of polymer).

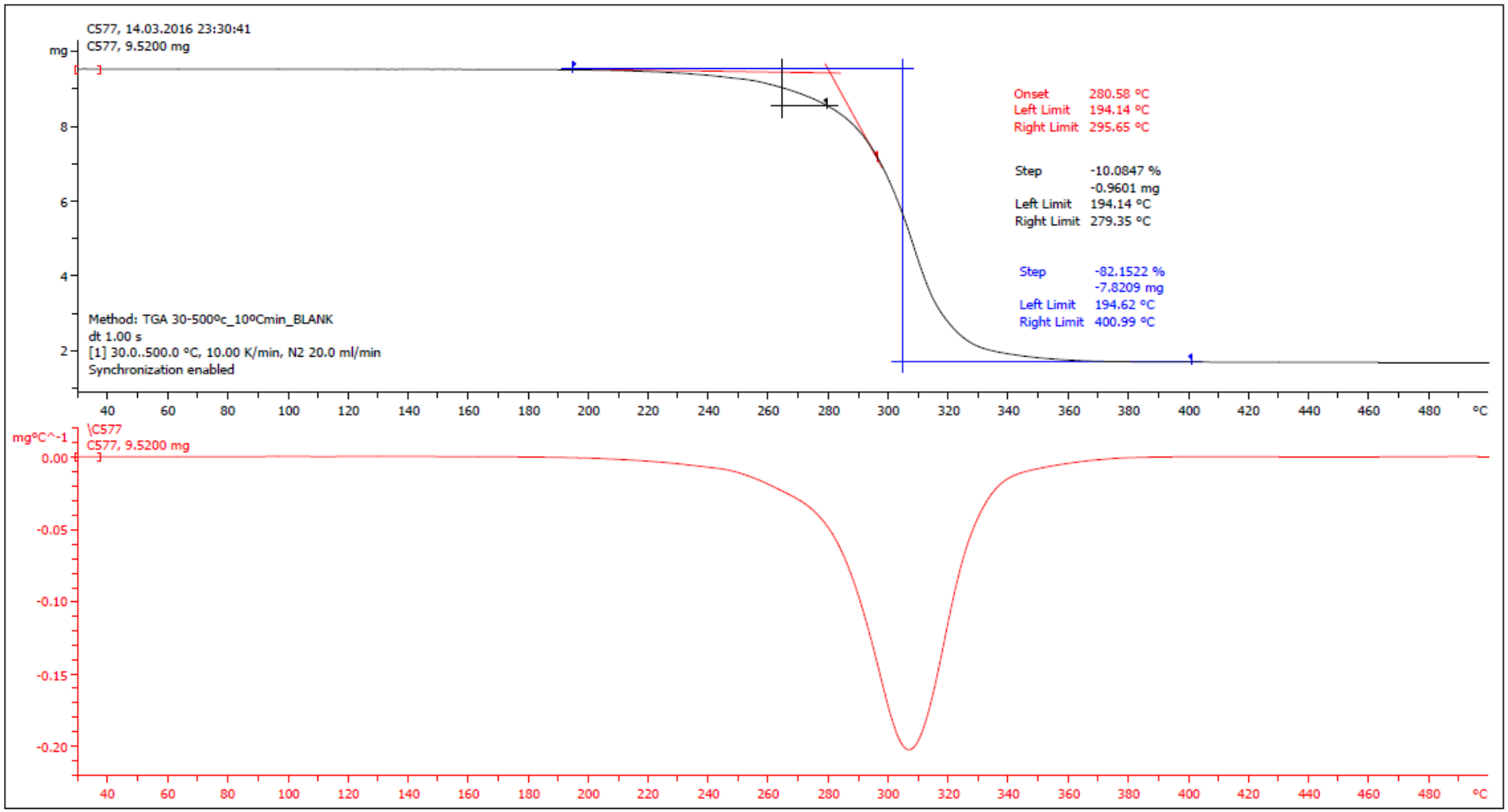


Figure S73. DSC analysis of the **CLP-20** (Table 3, entry 2). Shown are the DSC traces after a second, third and fourth cycle (T_g´s: 117.89, 118.22 and 118.22ºC, respectively).

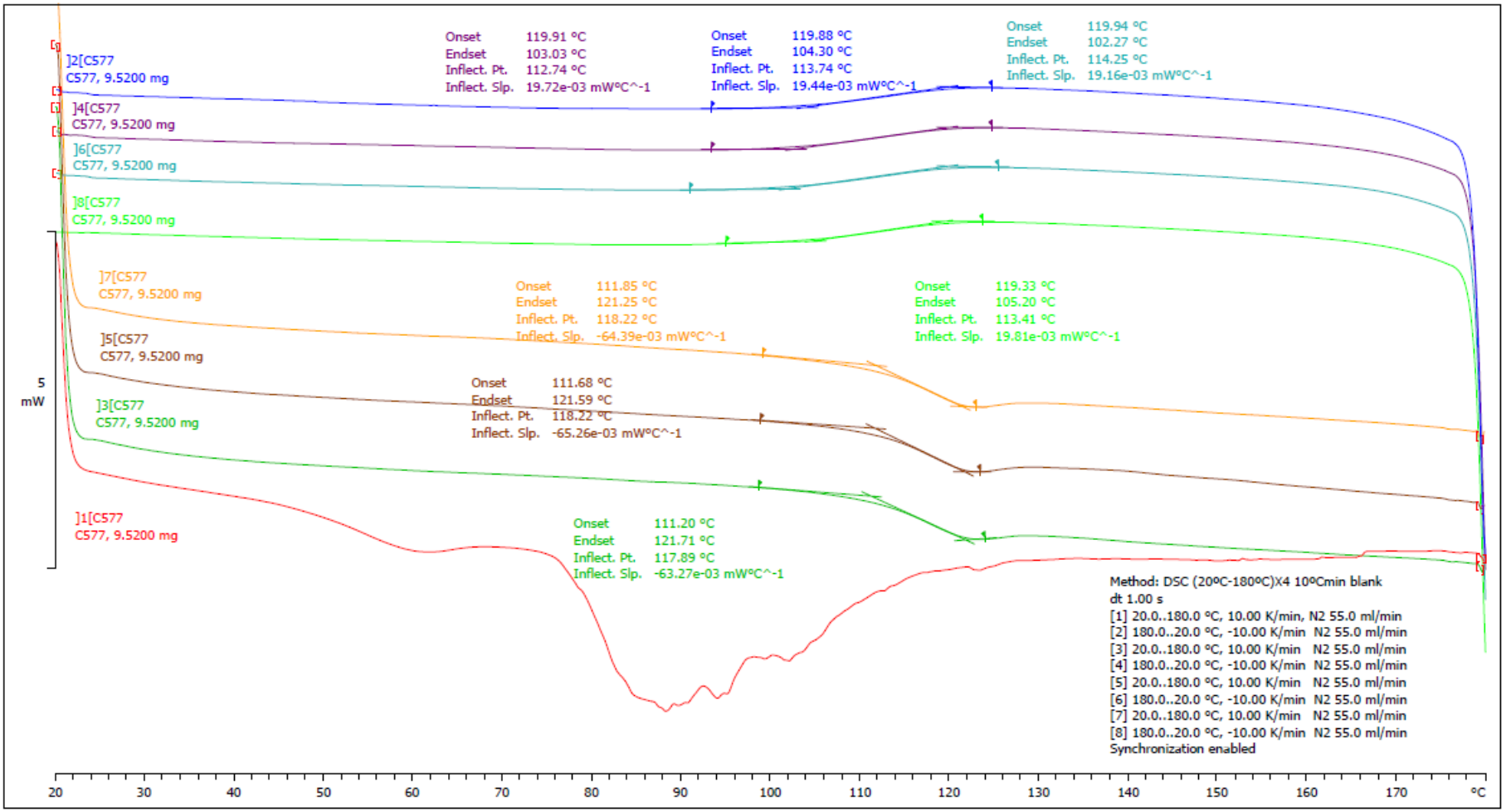


Figure S74. TGA of **CLP-30** (T_d = 263.84ºC at 10 % weight loss of polymer).

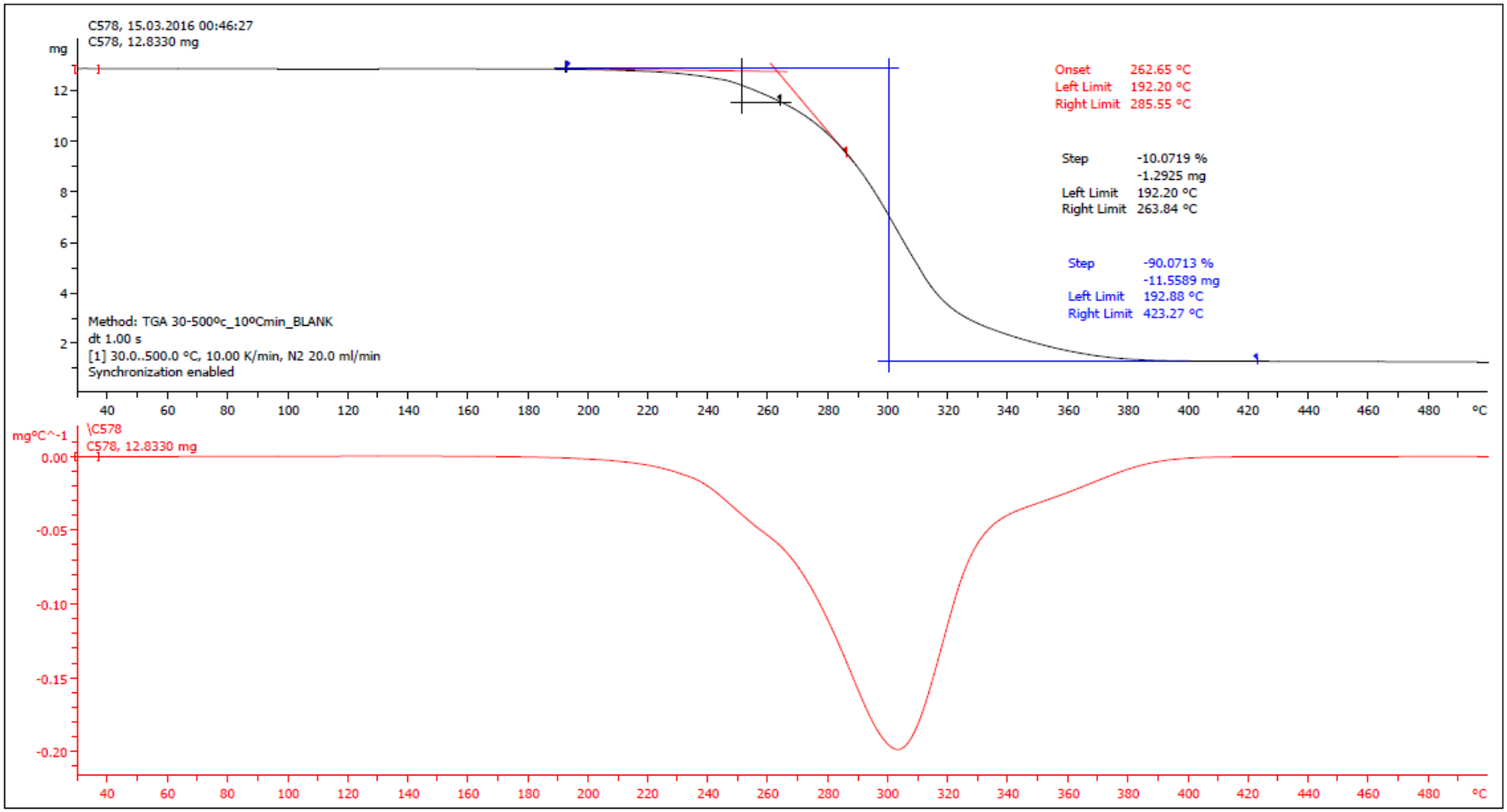


Figure S75. DSC analysis of the **CLP-30** (Table 3, entry 3). Shown are the DSC traces after a second, third and fourth cycle (T_g´s: 110.68, 116.01 and 113.51ºC, respectively).

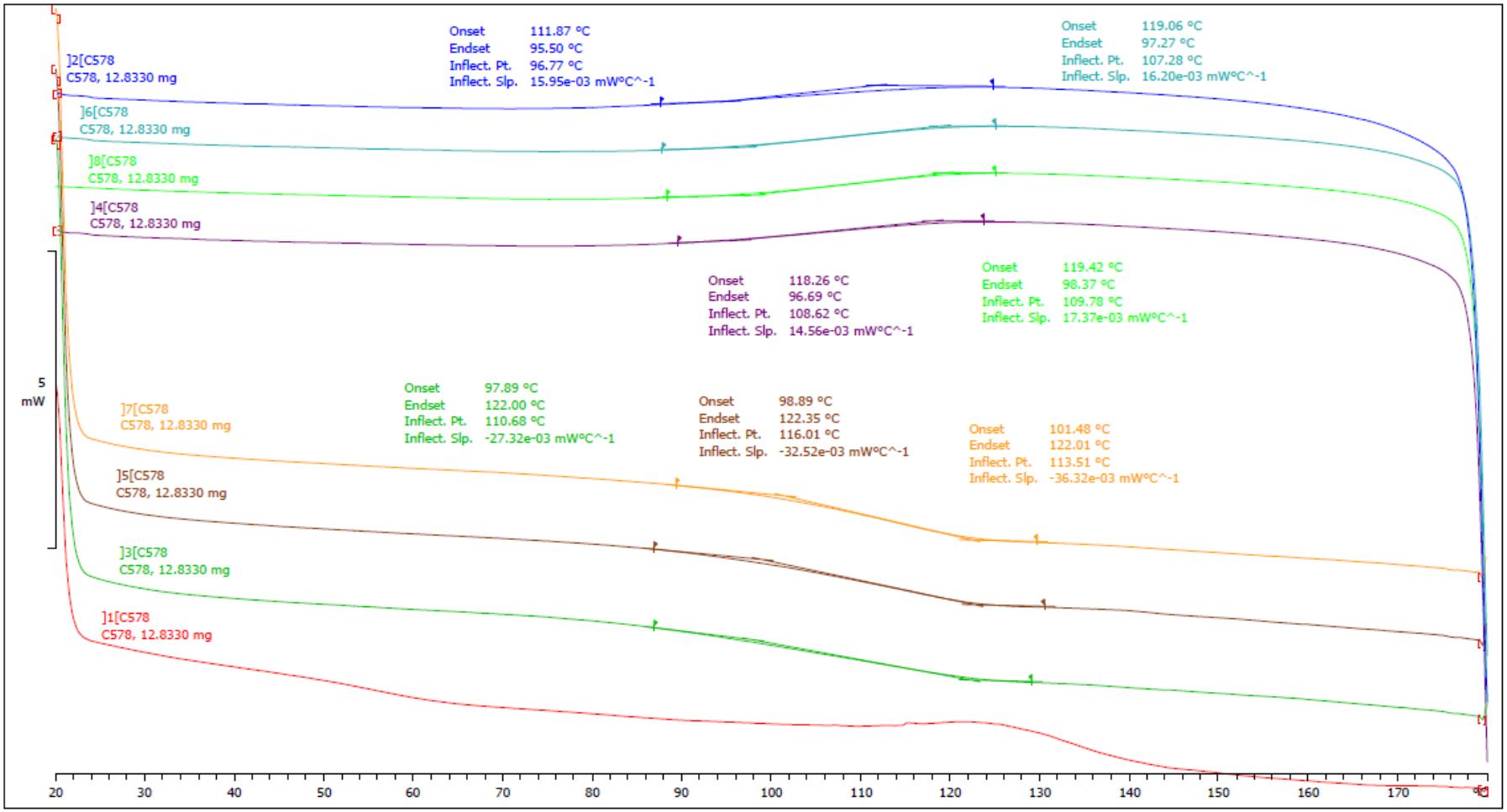


Figure S76. TGA of the **CLP-40** (T_d = 256.10 C at 10 % weight loss of polymer).

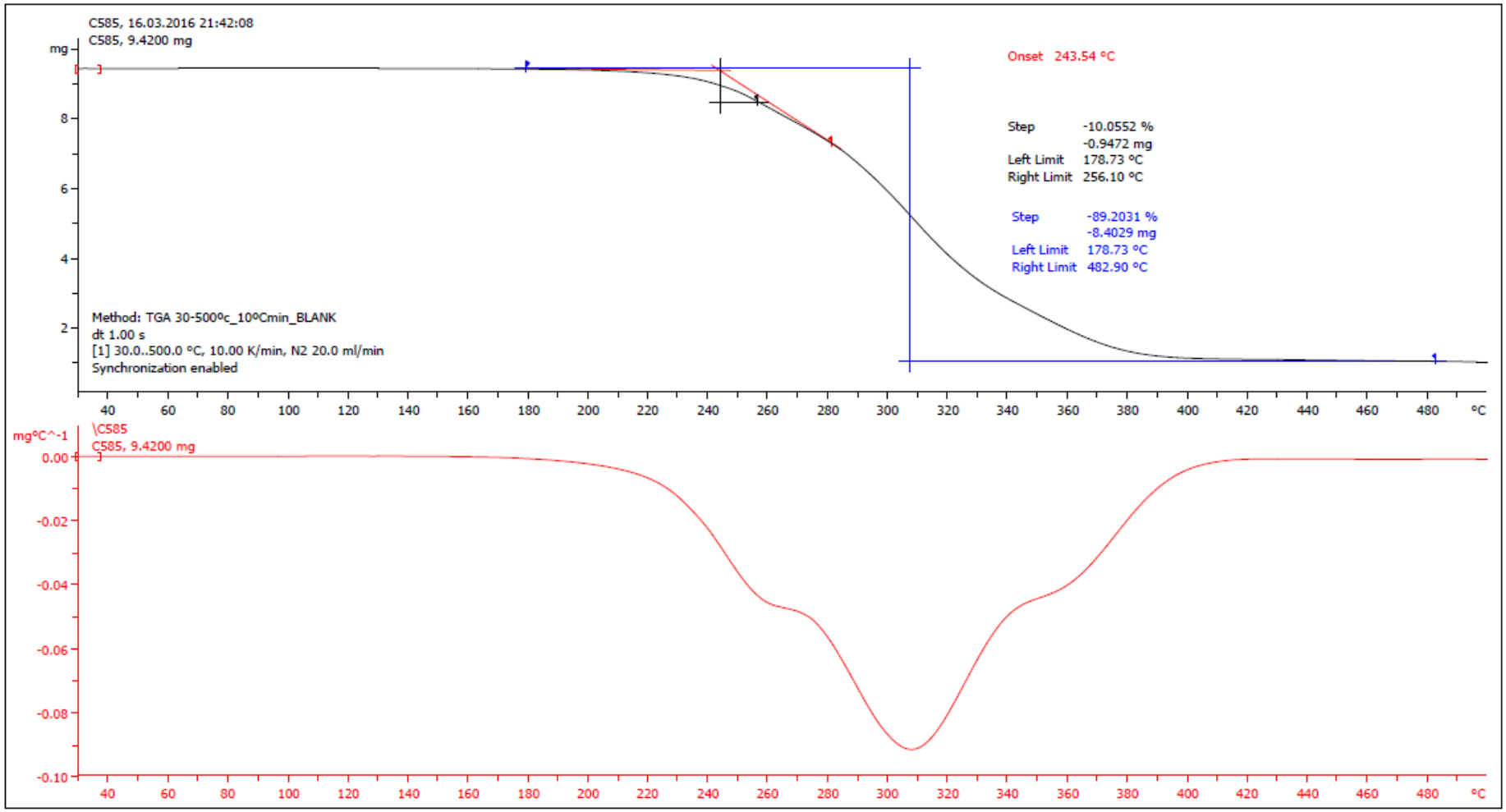


Figure S77. DSC analysis of the **CLP-40** (Table 3, entry 4). Shown are the DSC traces after a second, third and fourth cycle (T_g´s: 108.87, 121.19 and 118.69ºC, respectively).

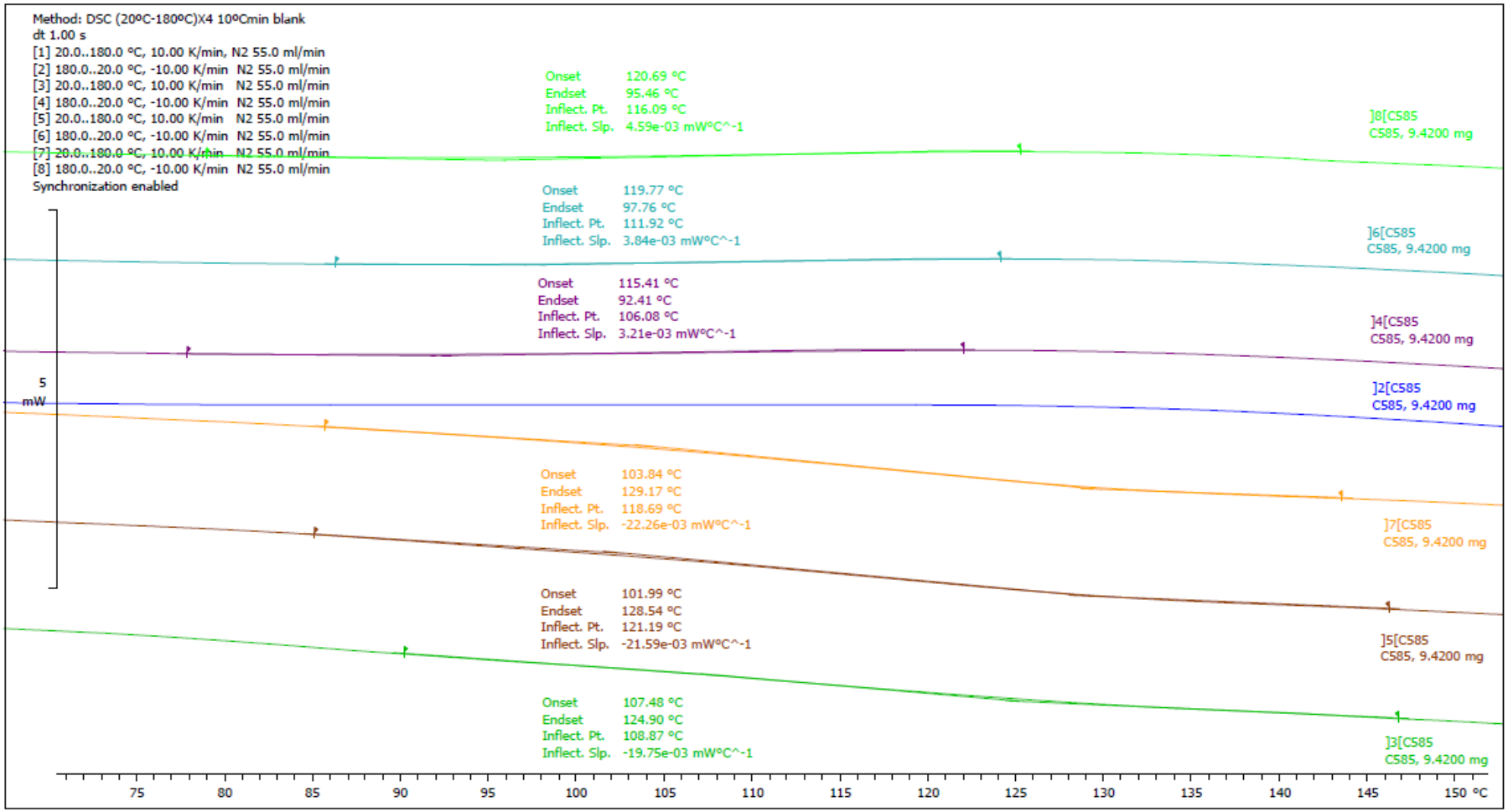


Figure S78. TGA of the **CLP-100** (T_d = 245.14ºC at 10 % weight loss of polymer).

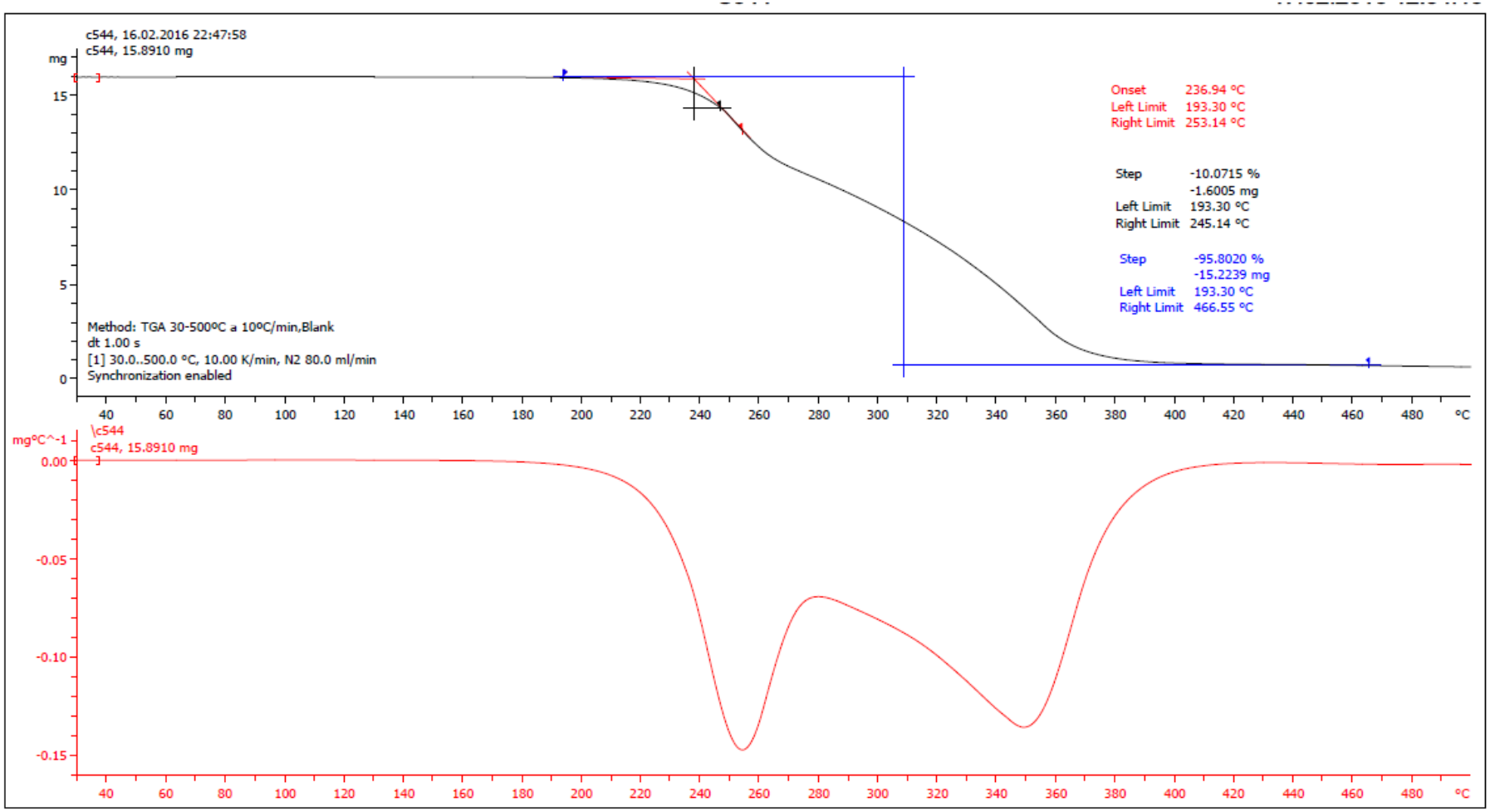


Figure S79. DSC analysis of the **CLP-100** (Table 3, entry 5). Shown are the DSC traces after a second and third cycle (T_g´s: 150.46 and 150.29ºC, respectively).

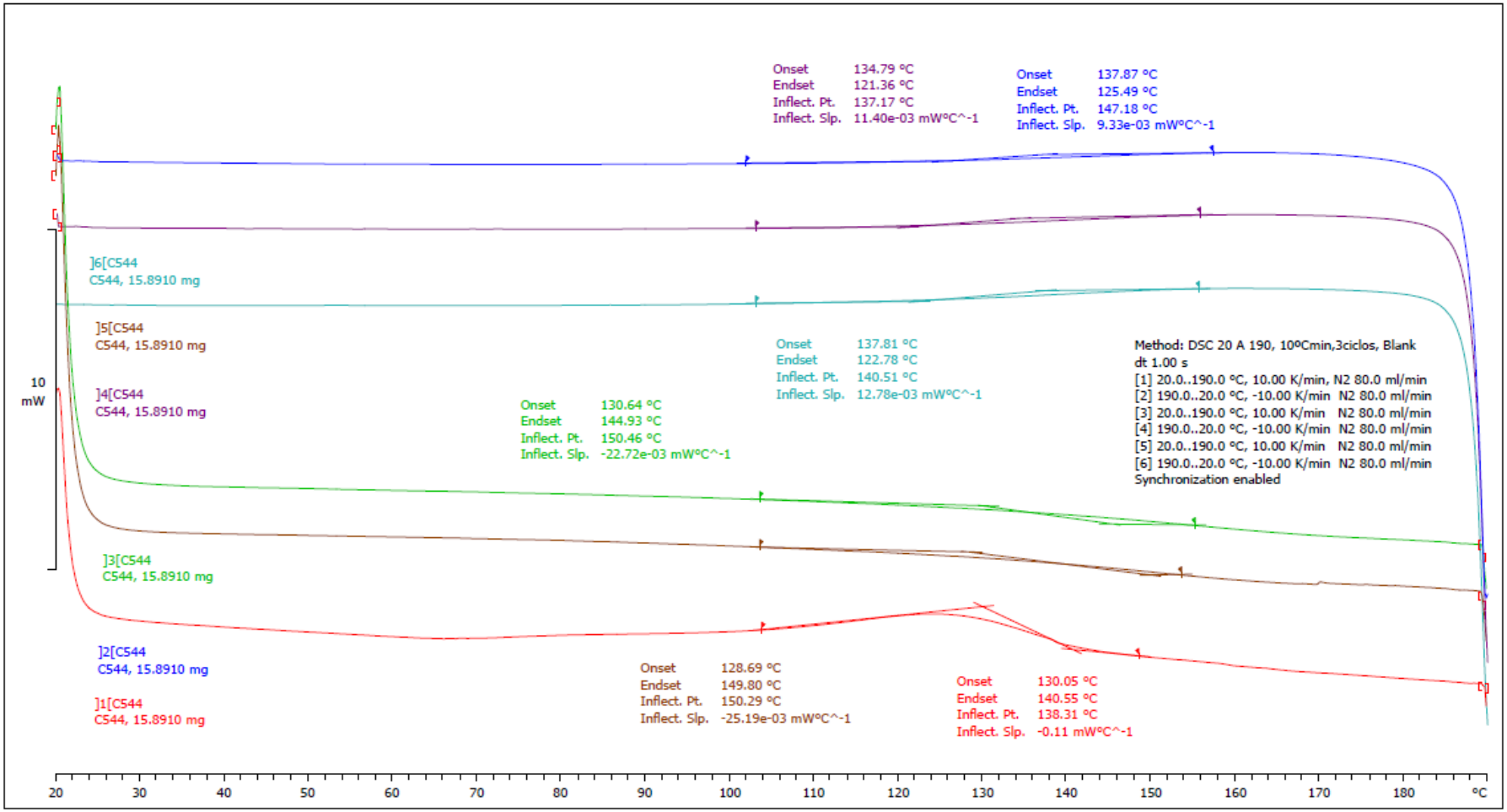


Figure S80. TGA of the **CLP-20a** (T_d = 264.30ºC at 10 % weight loss of polymer).

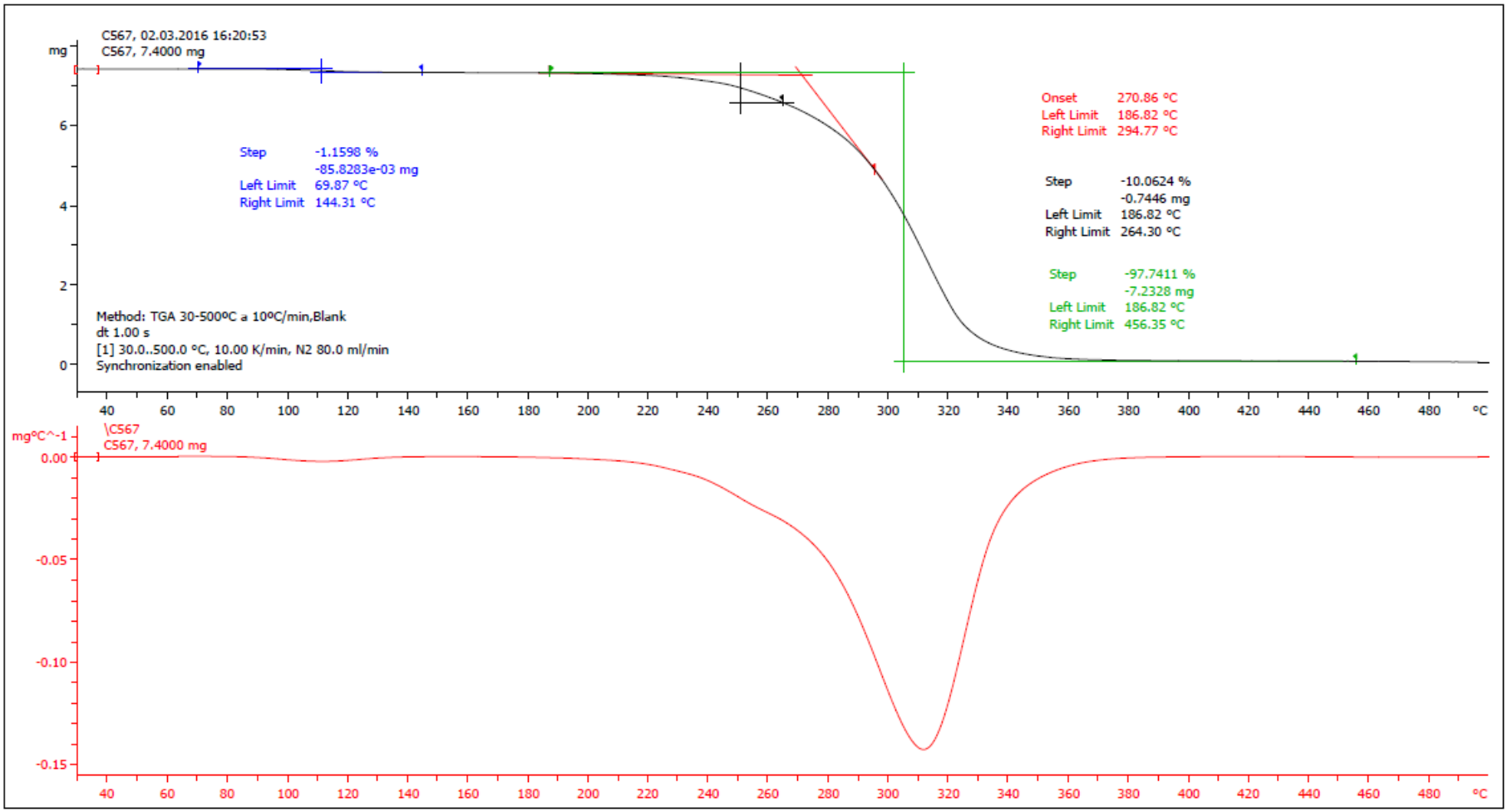


Figure S81. DSC analysis of the **CLP-20a** (Table 2, entry 1). Shown are the DSC traces after a second and third cycle (T_g´s: 105.22 and 107.05ºC, respectively).

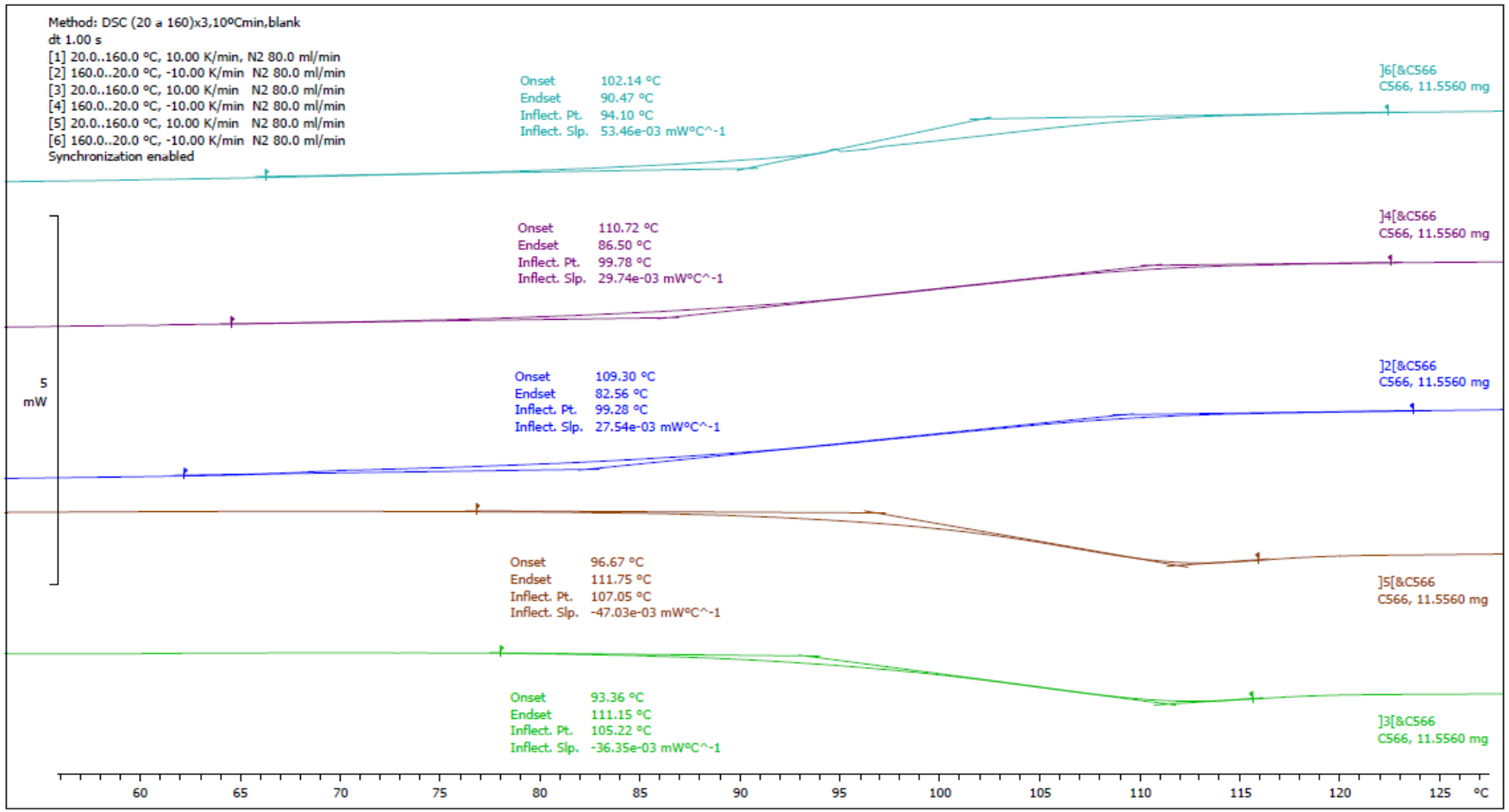


Figure S82. TGA of the **CLP-20b** (T_d = 271.63ºC at 10 % weight loss of polymer).

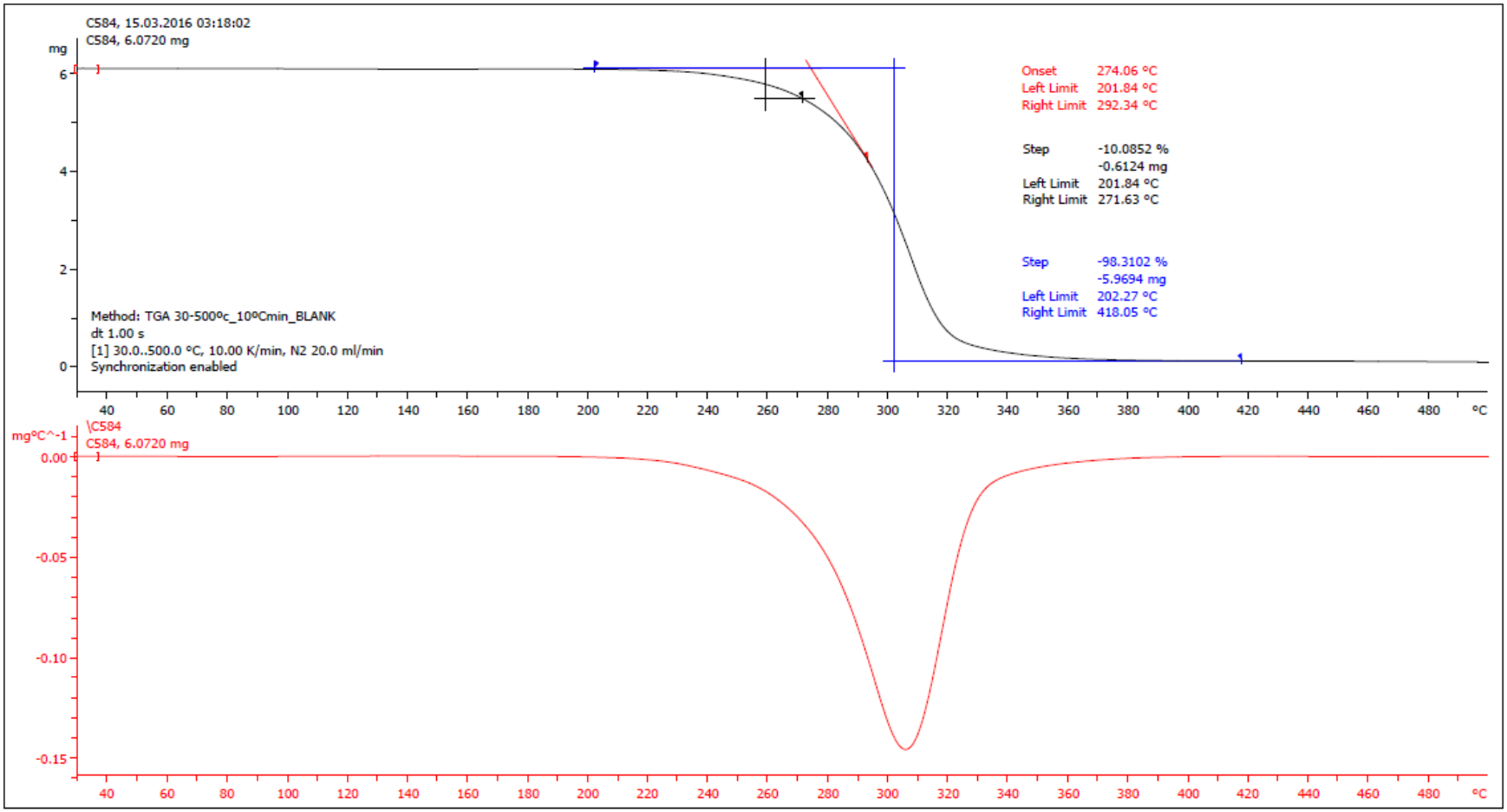


Figure S83. DSC analysis of the **CLP-20b** (Table 2, entry 1). Shown are the DSC traces after a second, third and fourth cycle (T_g´s: 109.75, 108.92 and 108.58ºC, respectively).

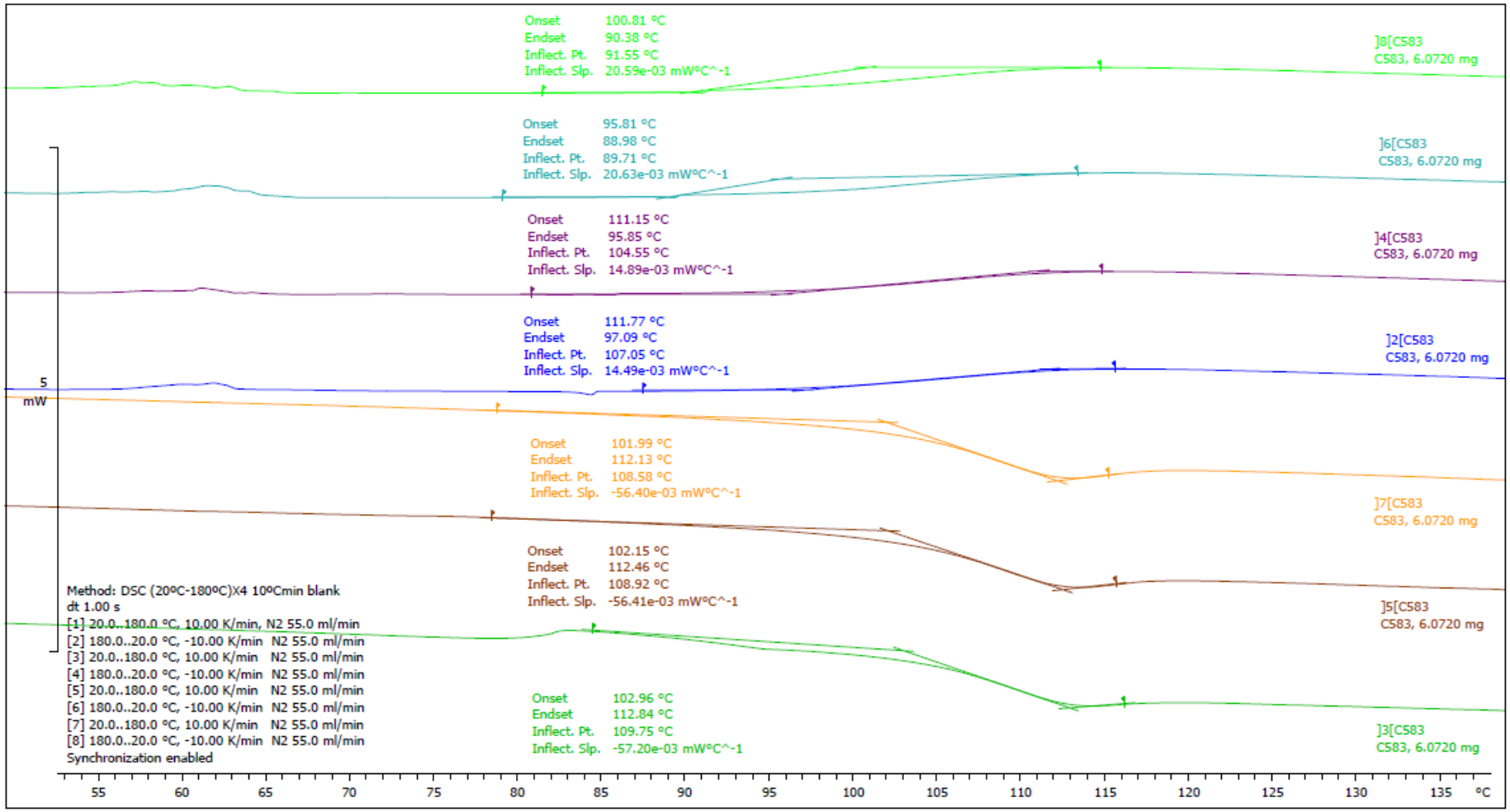


Figure S84. TGA of the **CLP-20d** (T_d = 271.58ºC at 10 % weight loss of polymer).

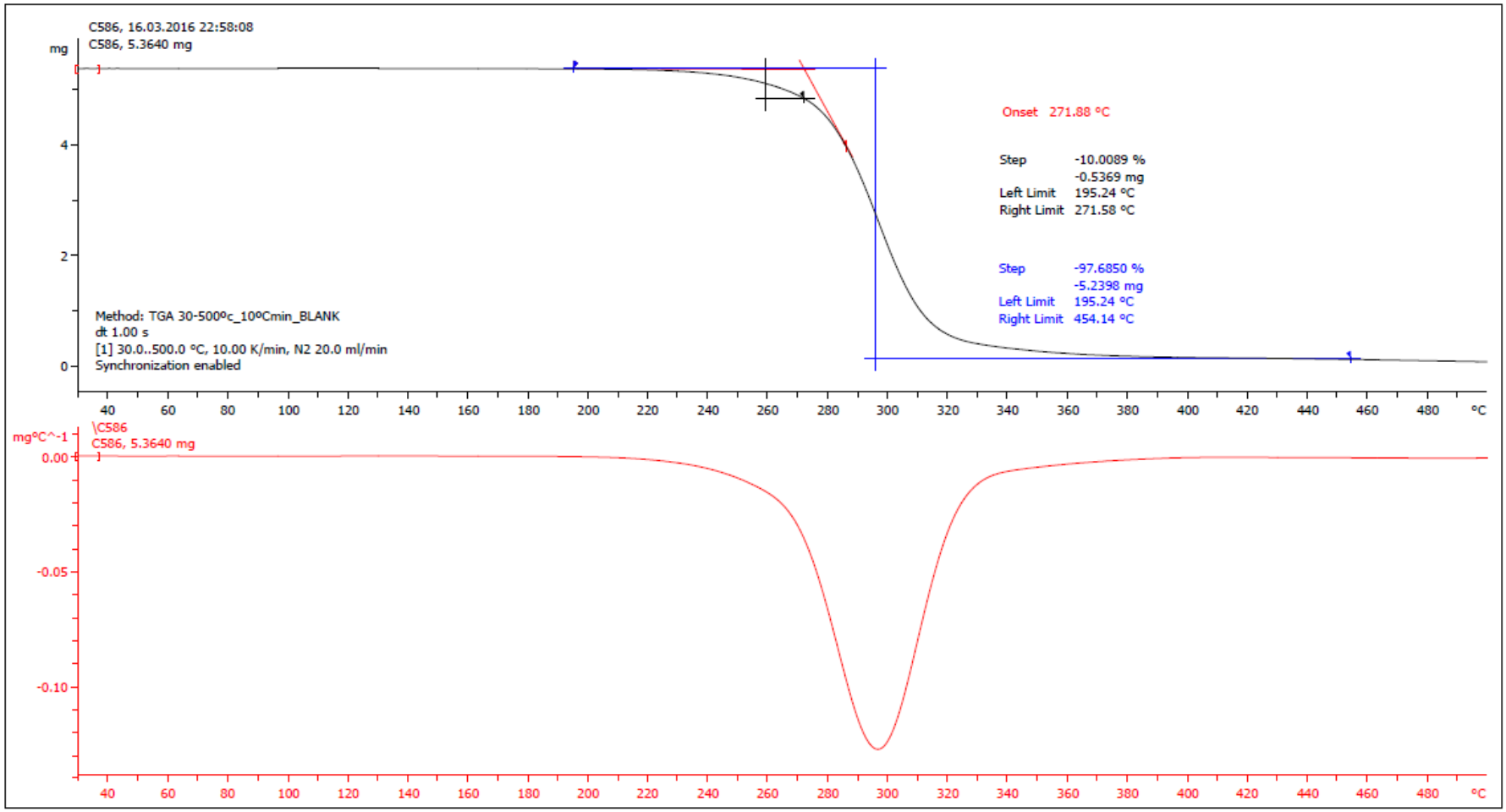


Figure S85. DSC analysis of the **CLP-20d** (Table 2, entry 3). Shown are the DSC traces after a second, third and fourth cycle (T_g´s: 112.55, 112.55 and 112.22ºC, respectively).

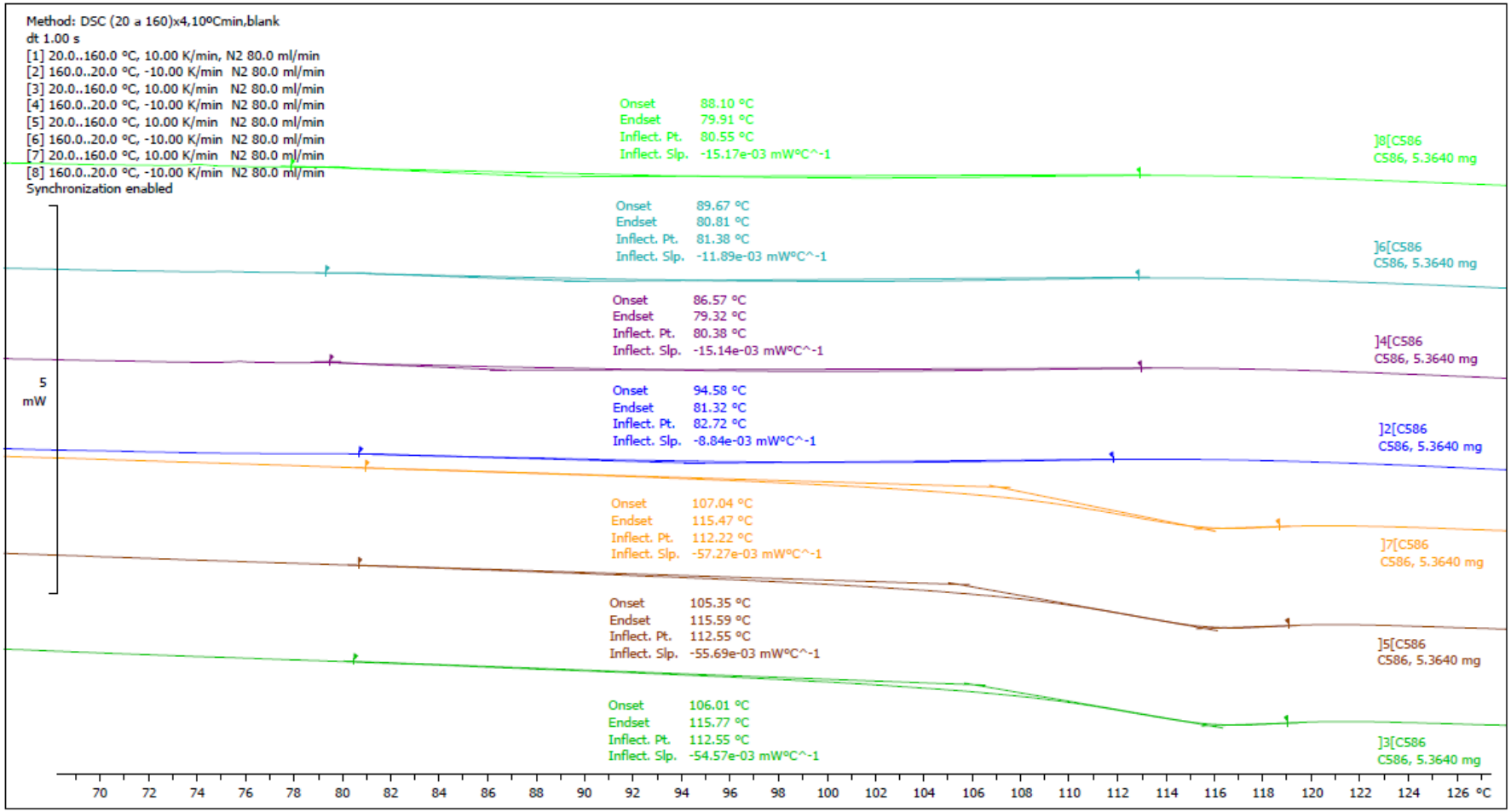


Figure S86. TGA of the **CLP-100a** (T_d = 238.61ºC at 10 % weight loss of polymer).

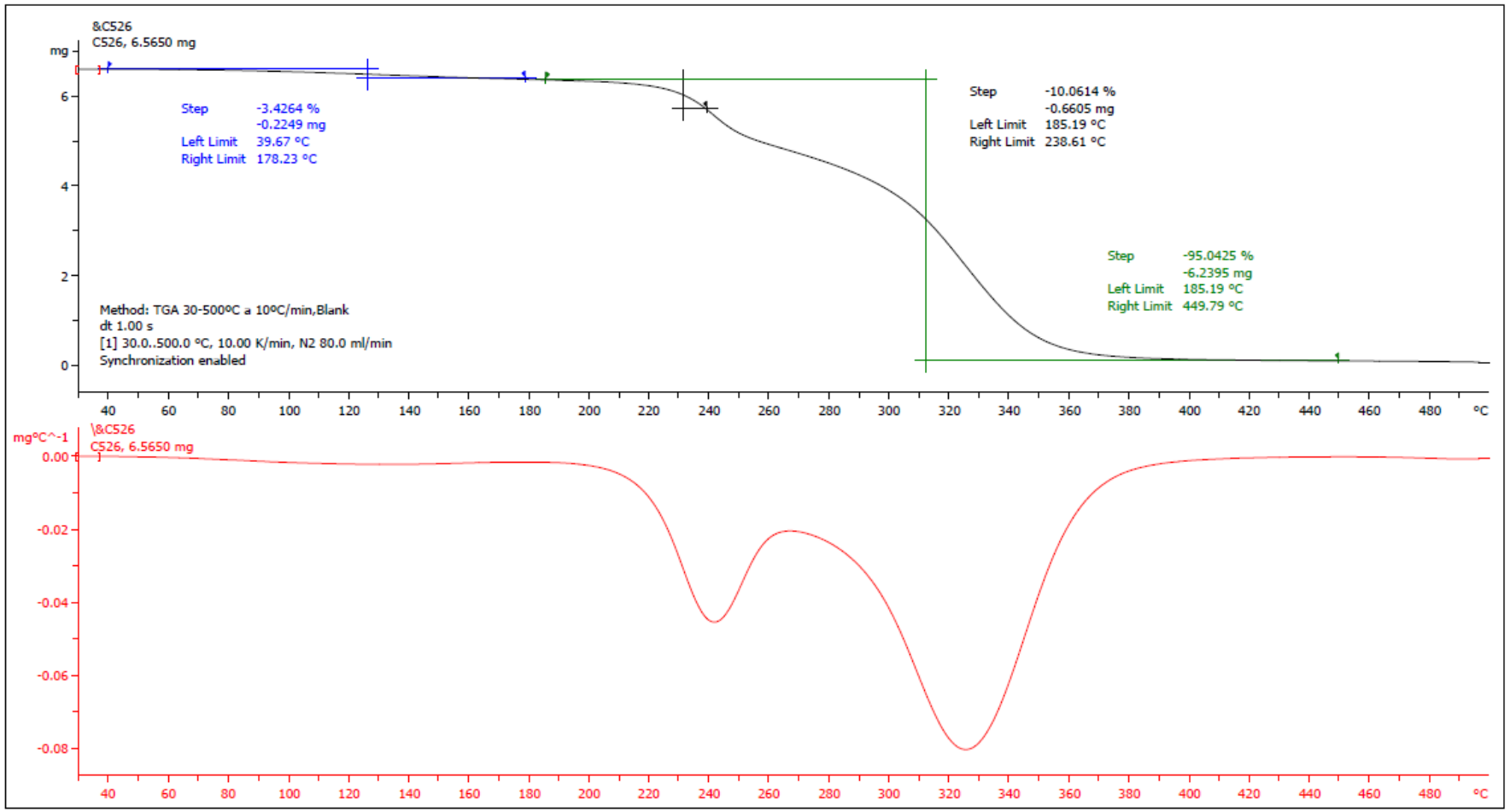


Figure S87. DSC analysis of the **CLP-100a** (Table 3, entry 6). Shown are the DSC traces after a second and third cycle (T_g´s: 83.73 and 83.23ºC, respectively).

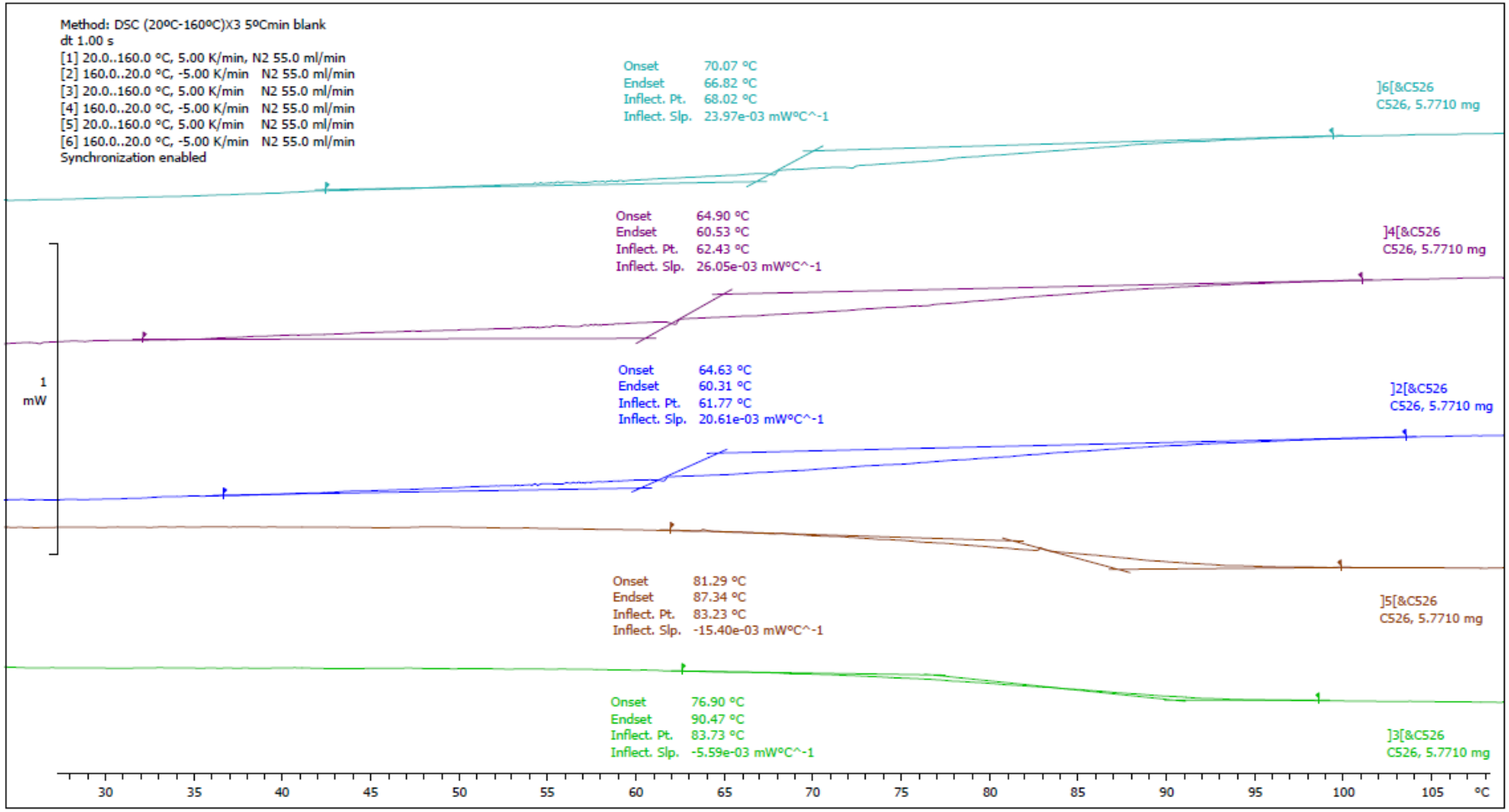


Figure S88. TGA of the **CLP-100b** (T_d = 232.85ºC at 10 % weight loss of polymer).

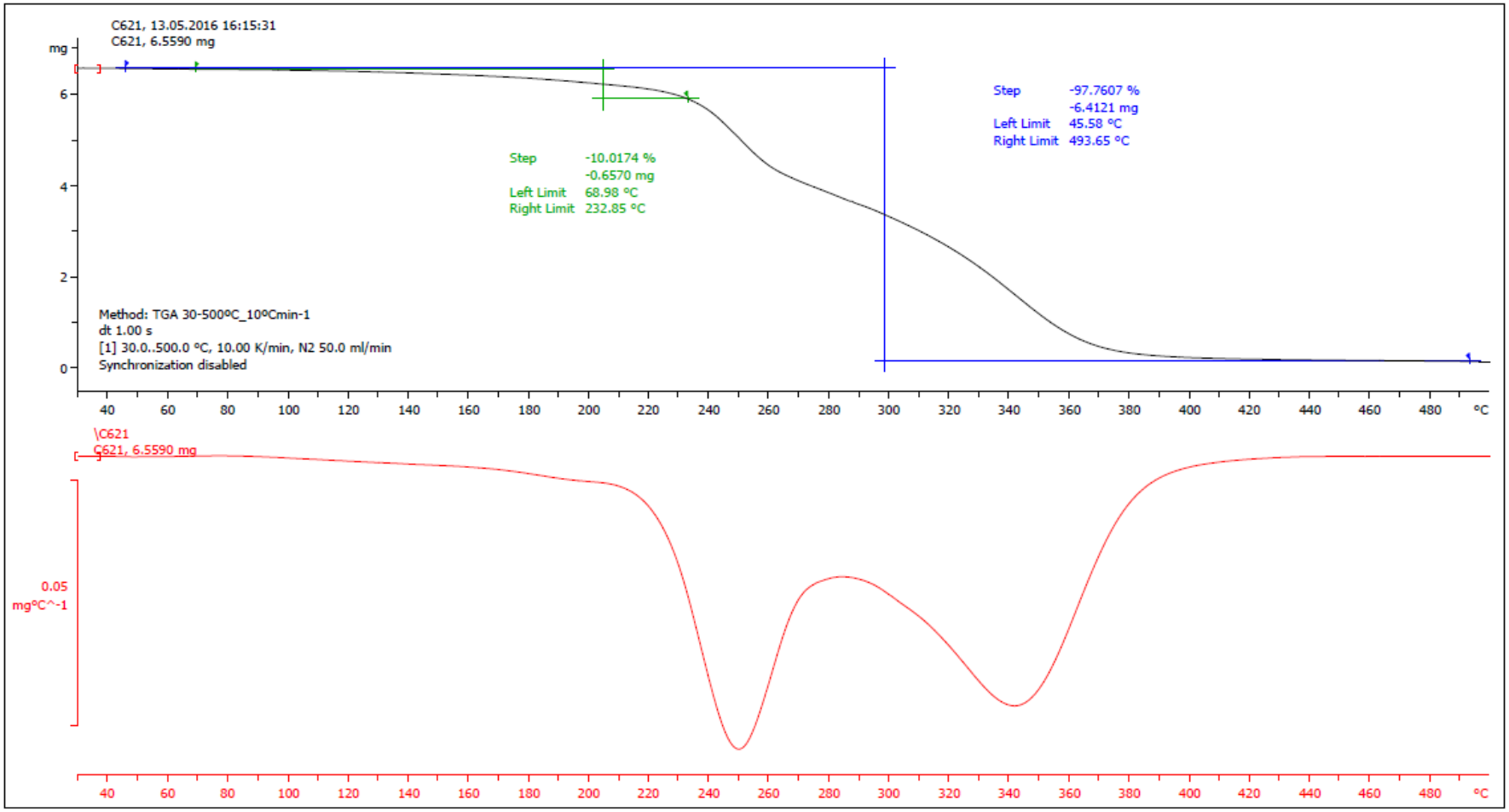
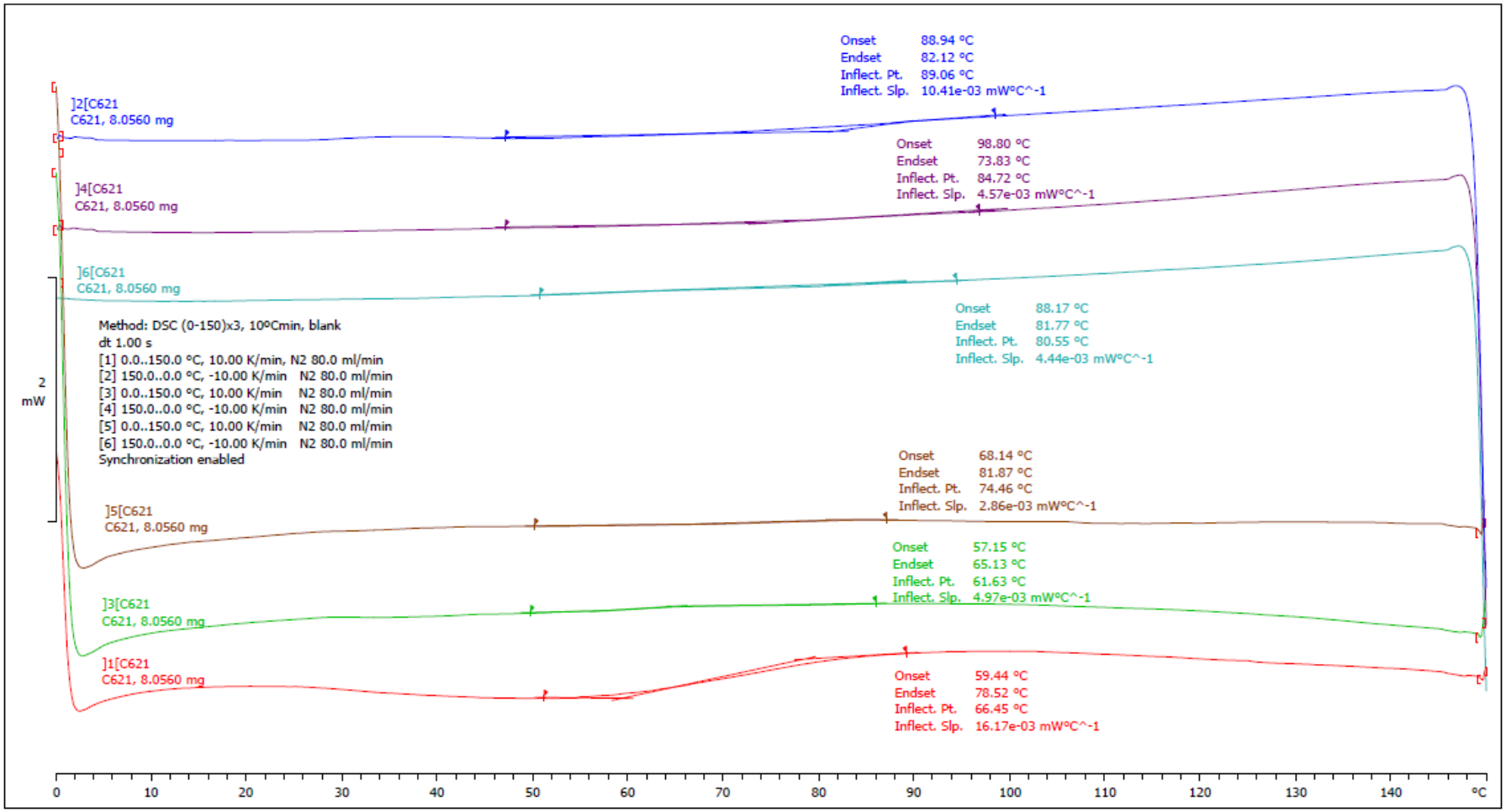


Figure S89. DSC analysis of the **CLP-100b** (Table 3, entry 7). Shown are the DSC traces after a second and third cycle (T_g´s: 61.63 and 74.46ºC, respectively).



ADDITIONAL KINETIC DATA:

Table S1. Remaining % of CHO and LO, and terpolymer conversion during the coupling process in time.

t (h)	CHO (%)	LO (%)	Terpolymer conv. (%)	LO incorporated (%)
2	76	97	14	12
3	63	93	22	17
4	45	85	35	22
5	23	79	49	21
6	13	76	55	22
9.5	1	69	65	24
24	0.3	65	68	25
48	0	62	70	26

Reaction conditions: 1:1 ratio of CHO and LO (3.5 mmol in total), $\mathbf{Al^{Me}}$ = 0.50 mol %, PPNCl = 0.25 mol %), $p(CO_2)^o$ = 15 bar, neat, T = 40ºC. Polycarbonate conversion, and amount of CHO and LO (%) were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,4-dimethoxybezene as internal standard (δ = 3.76 ppm).

Table S2. Relative CHO and LO consumption measured in time.

t (h)	mmol CHO	mmol LO	Δmmol CHO	Δmmol CHO	$\mathbf{mmol_{CHO}/mmol_{LO}}$
2	0.42	0.06	0.42	0.06	7.00
3	0.64	0.13	0.22	0.07	3.14
4	0.96	0.26	0.32	0.13	2.46
5	1.35	0.36	0.39	0.10	3.90
6	1.52	0.42	0.17	0.06	2.83
9.5	1.75	0.54	0.23	0.12	1.92
24	1.78	0.61	0.03	0.07	0.43
48	1.80	0.66	0.02	0.05	0.40

Reaction conditions: 1:1 ratio of CHO and LO (3.5 mmol in total), $\mathbf{Al^{Me}}$ = 0.50 mol %, PPNCl = 0.25 mol %), $p(CO_2)^o$ = 15 bar, neat, T = 40ºC. Polycarbonate conversion, and amount of CHO and LO (%) were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,4-dimethoxybezene as internal standard (δ = 3.76 ppm).

TABLES CONTAINING ADDITIONAL INFORMATION:

Table S3. Reproducibility data for the terpolymerization processes.

Terpolymer	Conversion	LO incorporated (%)	T_g (ºC)
T-10	70	10	111
	79	13	102
	70	11	102
T-20	68	17	109
	71	20	100
	77	20	103
T-30	75	32	96
	75	29	100
	79	33	95
T-40	73	42	83
	73	42	89
	79	42	97

Table S4. Reproducibility data for the cross-linking reactions.

Cross-Linked Polymer	Solubility in organic solvent	T_g (°C)	ΔT_g (°C)
CLP-10	yes	117	15
	yes	118	16
CLP-20	yes	118	18
	yes	115	15
CLP-30	no	116	17
	no	113	13
CLP-40	no	119	22
	no	111	14
CLP-100	no	~150	~70
	no	~150	~70

PHOTOGRAPH OF THE REACTOR USED:

Figure S90. Standard autoclave used for the copolymerization reaction between CO_2 and epoxide(s).

REFERENCES:

(1) The NMR assignment (in ^{1}H and ^{13}C NMR spectra) was done using 2D experiments (COSY and HSQC), and the results compared with similar compounds in the literature, see for instance: Claudino, M.; Mathevet, J.-M.; Jonsson, M.; Johansson, M. *Polym. Chem.* **2014**, *5*, 3245–3260.