

Design and Characterization of Model Linear Low-Density Polyethylenes (LLDPEs) by Multi-Detector Size Exclusion Chromatography

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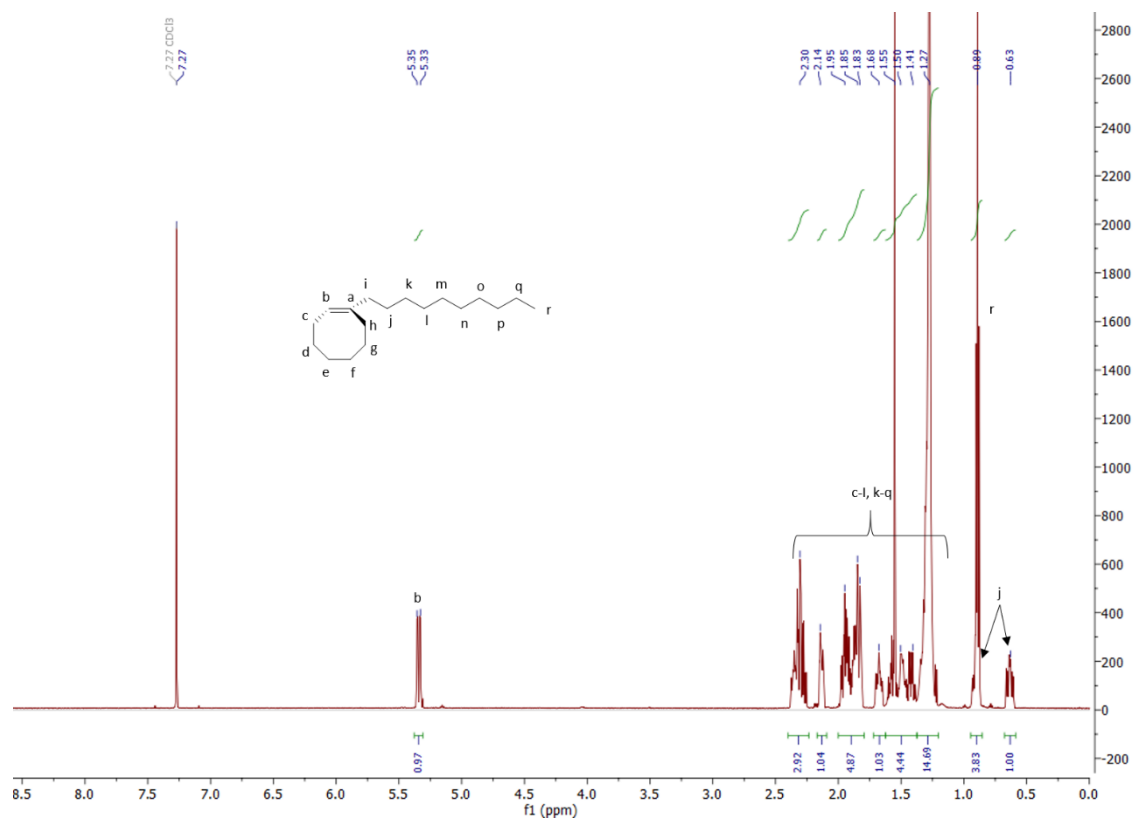


Figure S1. ^1H NMR (600 MHz, CDCl_3 , 25 $^\circ\text{C}$) of 1-decyl-*trans*-cyclooctene monomer.

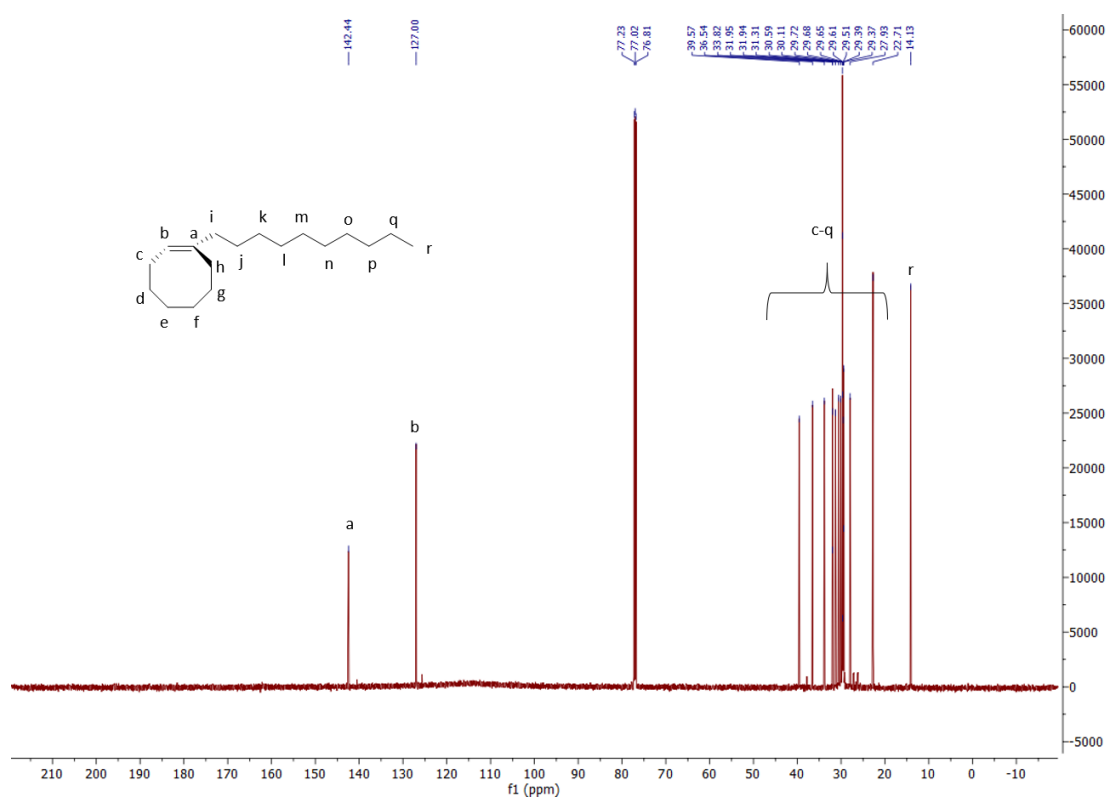


Figure S2. ^{13}C NMR (150 MHz, CDCl_3 , 25 $^\circ\text{C}$) of 1-decyl-*trans*-cyclooctene monomer.

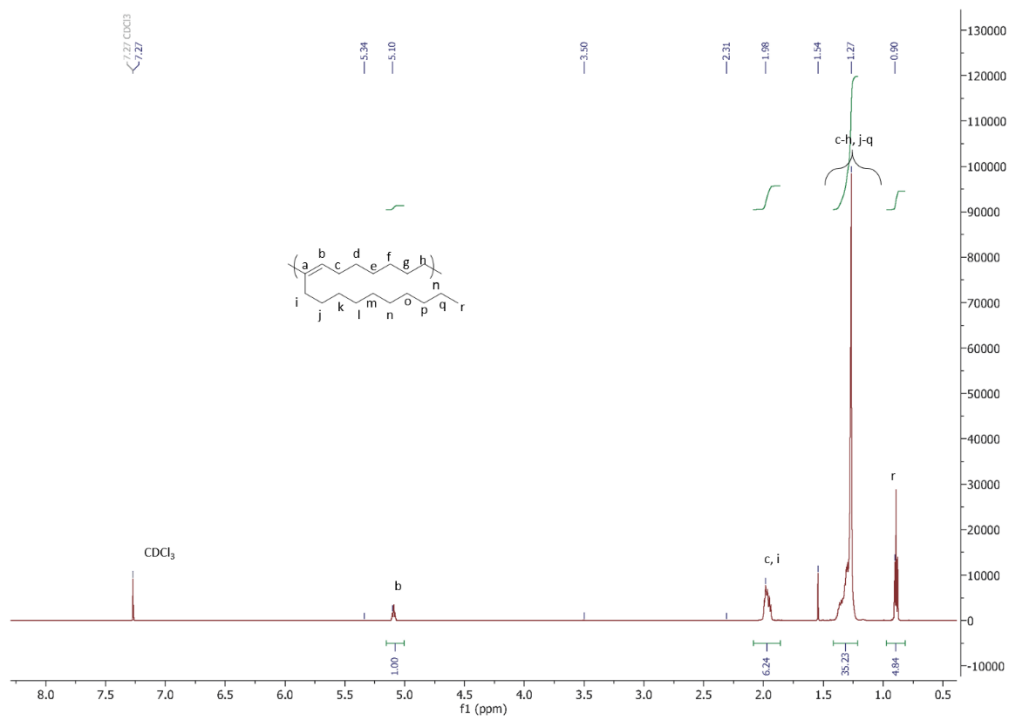


Figure S3. ^1H NMR (600 MHz, CDCl_3 , 25 $^\circ\text{C}$) of poly(1-decyl-*trans*-cyclooctene).

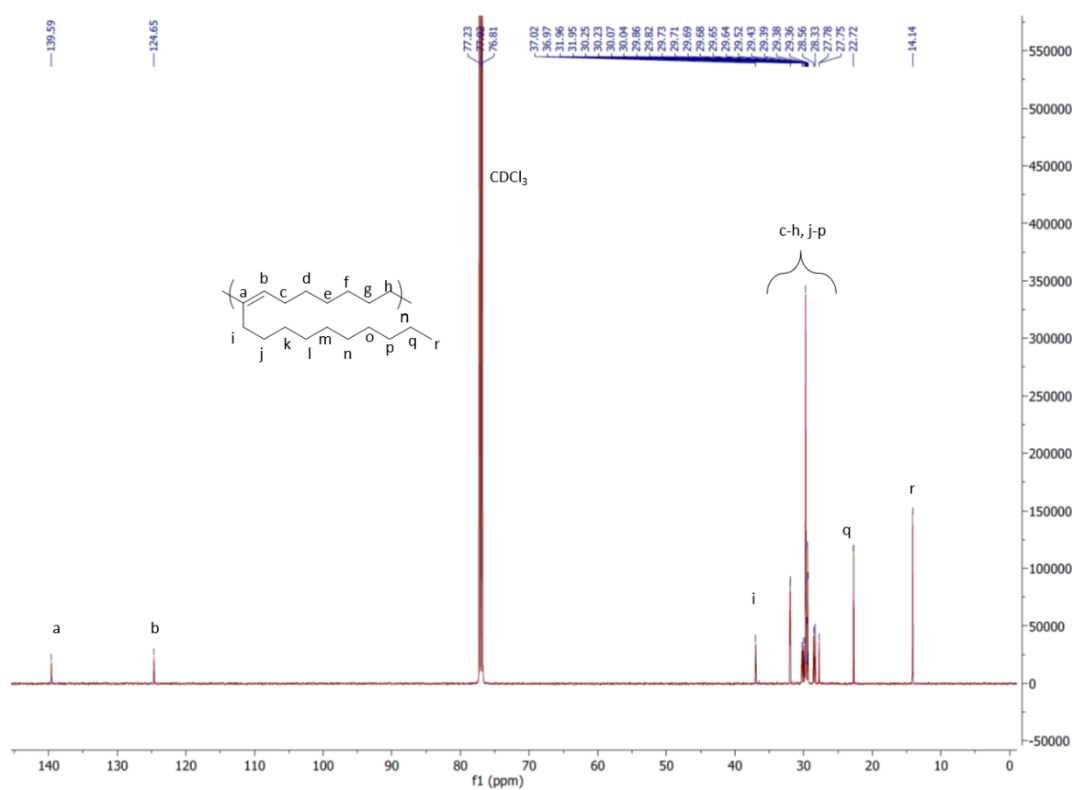


Figure S4. ^{13}C NMR (150 MHz, CDCl_3 , 25 $^\circ\text{C}$) of poly(1-decyl-*trans*-cyclooctene).

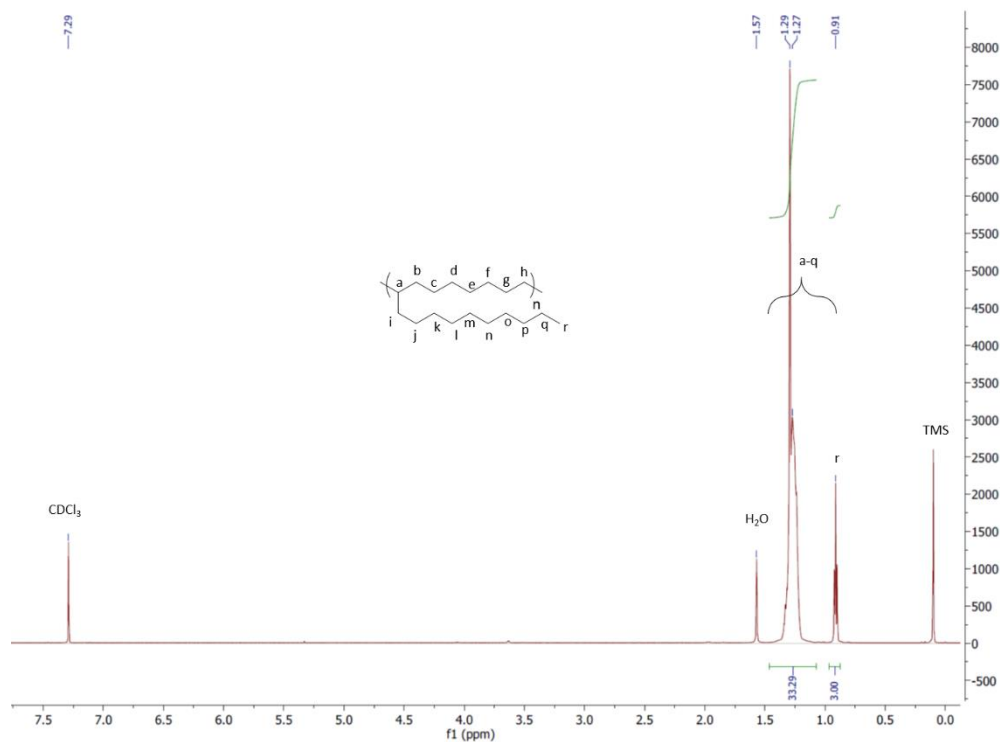


Figure S5. ¹H NMR (600 MHz, CDCl₃, 25 °C) of hydrogenated poly(1-decyl-*trans*-cyclooctene), (C10).

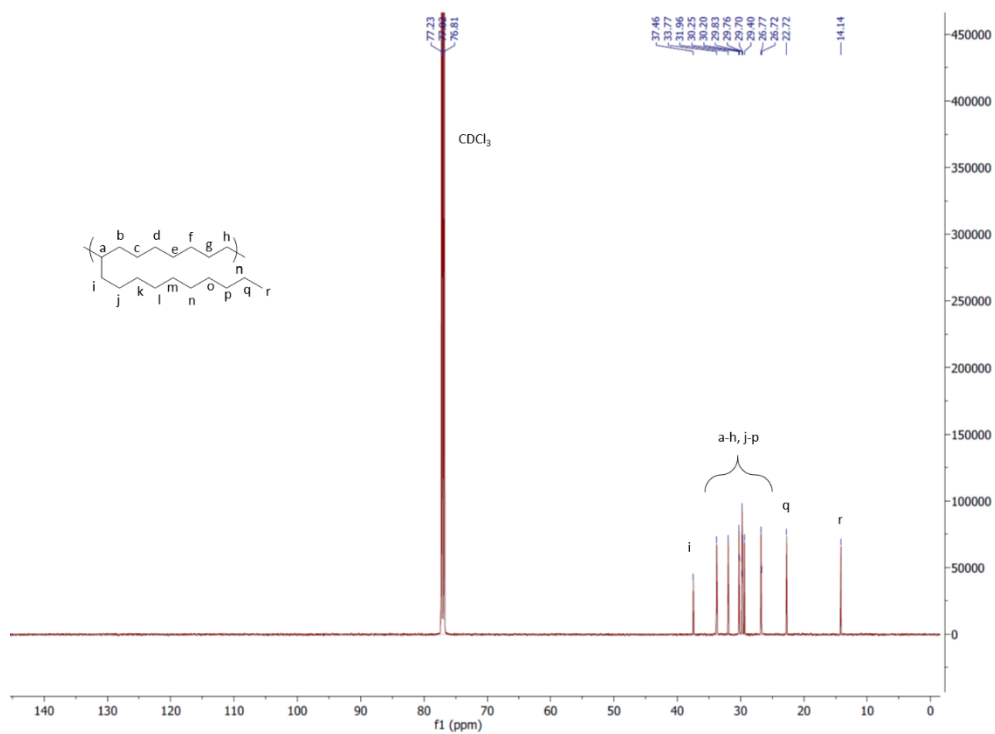


Figure S6. ¹³C NMR (150 MHz, CDCl₃, 25 °C) of hydrogenated poly(1-decyl-*trans*-cyclooctene), (C10).

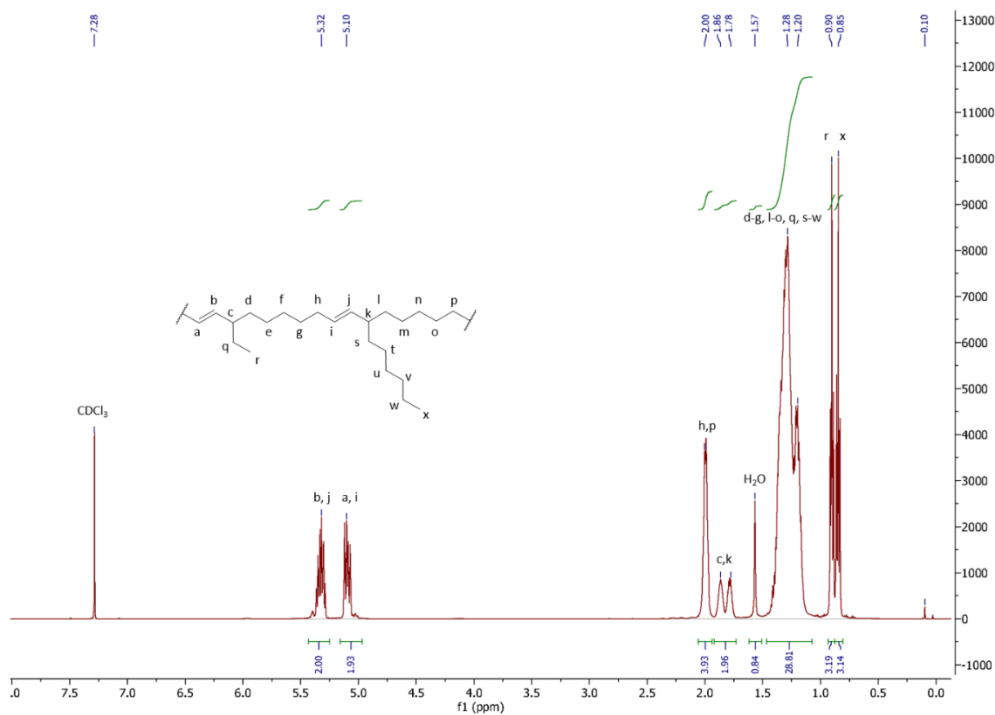


Figure S7. ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of poly(C2-stat-C6) polymer. The structure shown is a single 3-ethyl-*cis*-cyclooctene monomer adjacent to a 3-hexyl-*cis*-cyclooctene to highlight the chemical shifts of the statistical copolymer.

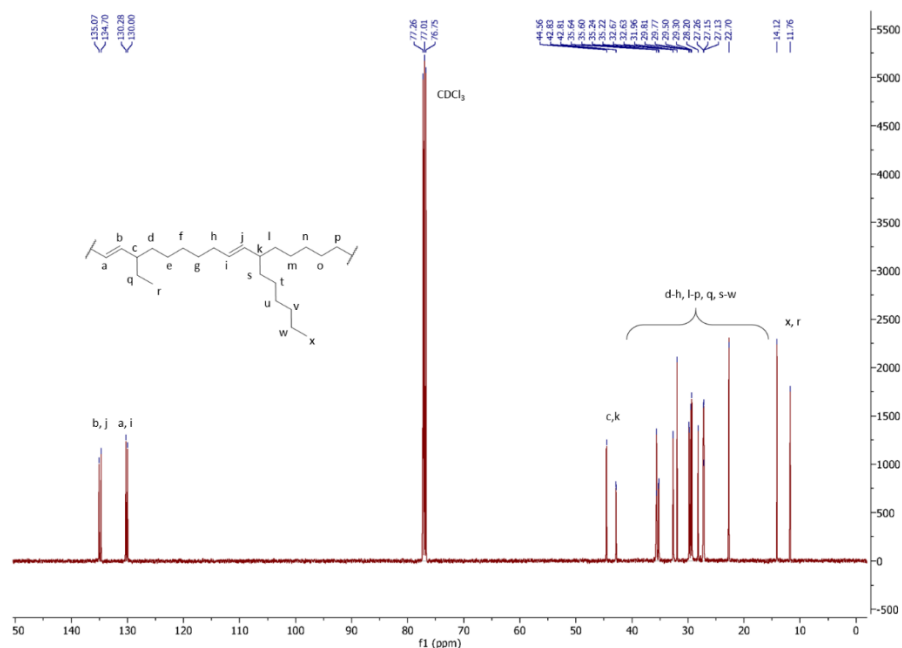


Figure S8. ^{13}C NMR (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) of poly(C2-stat-C6) polymer. The structure shown is a single 3-ethyl-*cis*-cyclooctene monomer adjacent to a 3-hexyl-*cis*-cyclooctene to highlight the chemical shifts of the statistical copolymer.

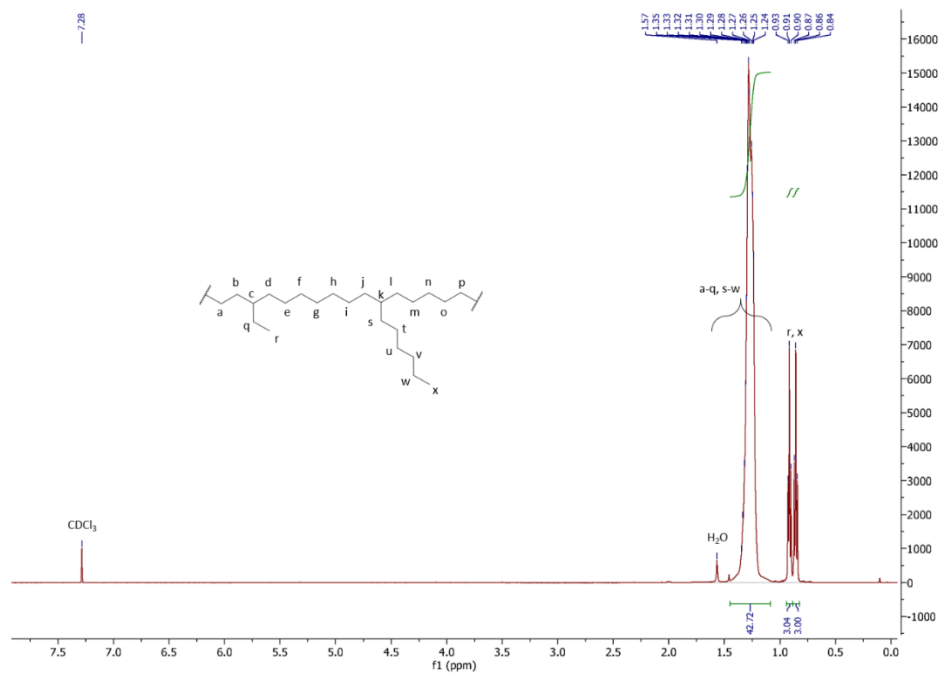


Figure S9. ¹H NMR (500 MHz, CDCl₃, 25 °C) of hydrogenated poly(C2-stat-C6) polymer.

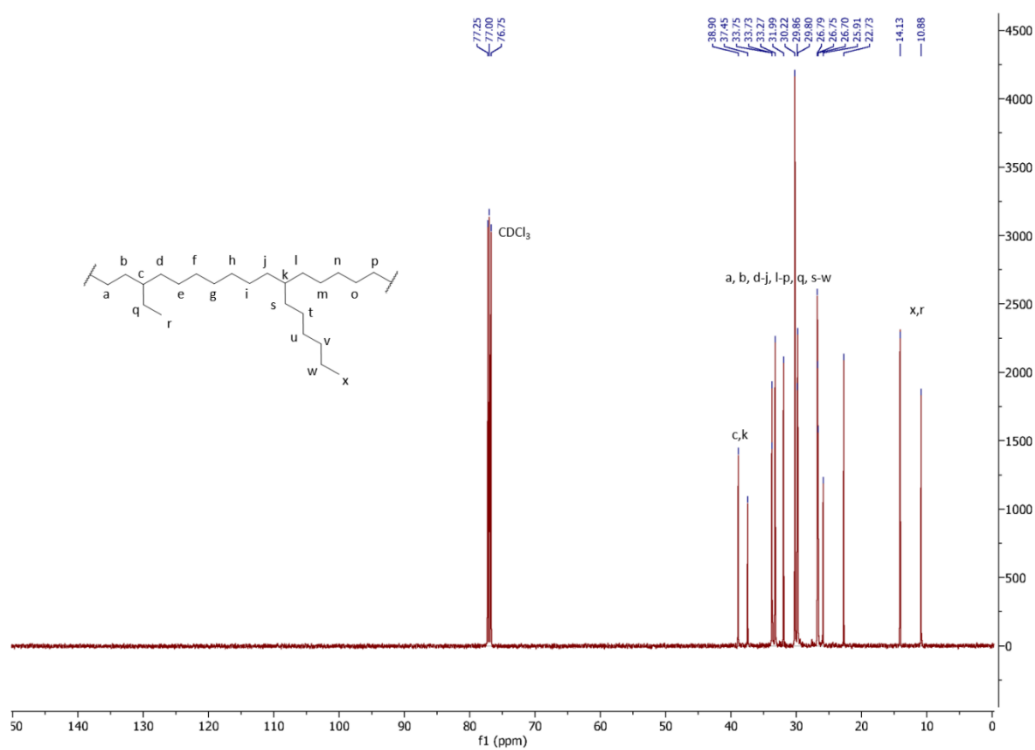


Figure S10. ¹³C NMR (125 MHz, CDCl₃, 25 °C) of hydrogenated poly(C2-stat-C6) polymer.

SEC Chromatograms

Ambient SEC chromatogram data are represented by the voltage response from differential refractive index detector (black), differential viscometer (differential pressure channel, purple), and 90° light scattering (green). High temperature SEC data are represented by the voltage response from differential RI detector (normalized, black), IR detector (alkyl signal: red, methyl signal: orange), specific viscosity (purple), and 90° light scattering (green). The secondary peak at ~29.5 mL is dodecane, a flow rate marker added to each sample.

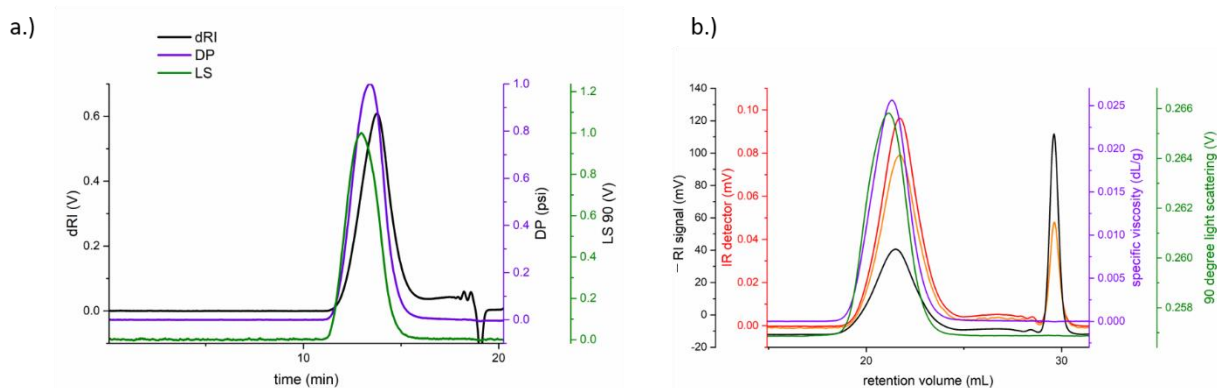


Figure S11. Representative SEC chromatograms for methyl (C1) branched LLDPE: a) ambient SEC (THF, 35 °C) and b) HT-SEC (1,2,4-trichlorobenzene (TCB), 135 °C). Low molar mass oligomers (broad secondary peak) were estimated to represent $10\% \pm 0.1\%$ of the total concentration, as calculated by HT-SEC RI detection.

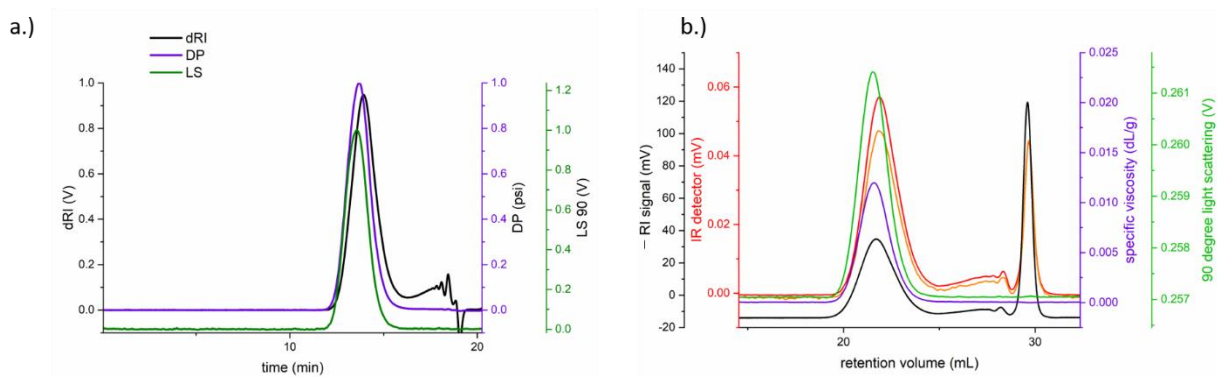


Figure S12. Representative SEC chromatograms for ethyl (C2) branched LLDPE: a) ambient SEC (THF, 35 °C) and b) HT-SEC (TCB, 135 °C). Low molar mass oligomers (broad secondary peak) were estimated to represent $14\% \pm 0.1\%$ of the total concentration, as calculated by HT-SEC RI detection.

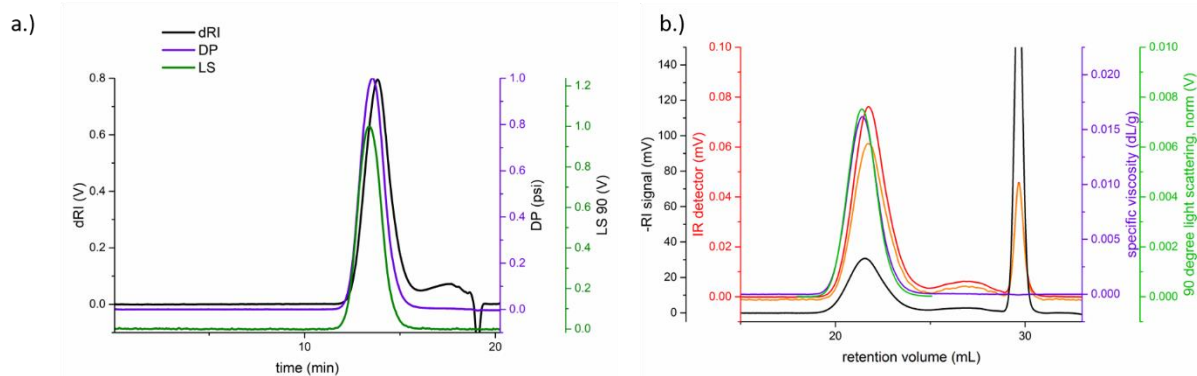


Figure S13. Representative SEC chromatograms for ethyl-co-hexyl (C2-co-C6) branched LLDPE: a) ambient SEC (THF, 35 °C) and b) HT-SEC (TCB, 135 °C). Low molar mass oligomers (broad secondary peak) were estimated to represent $14\% \pm 3.5\%$ of the total concentration, as calculated by HT-SEC RI detection.

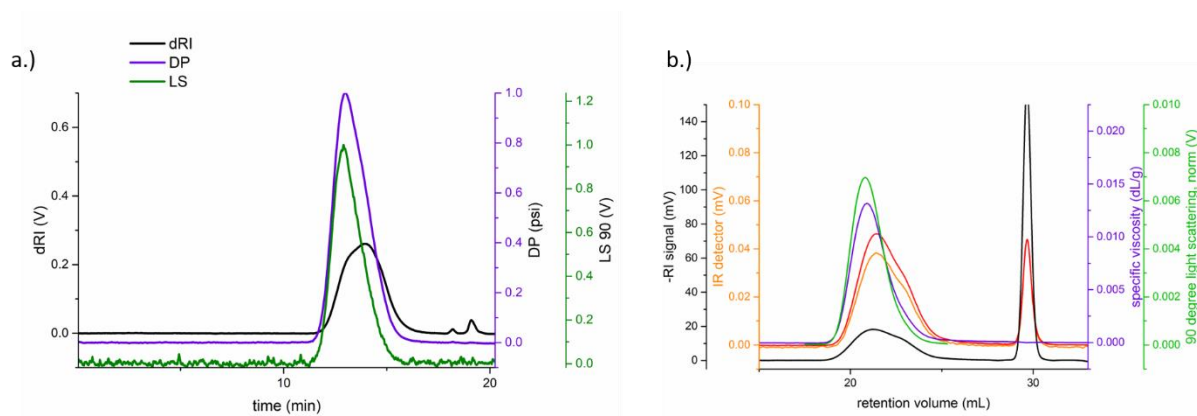


Figure S14. Representative SEC chromatograms for butyl (C4) branched LLDPE: a) ambient SEC (THF, 35 °C) and b) HT-SEC (TCB, 135 °C).

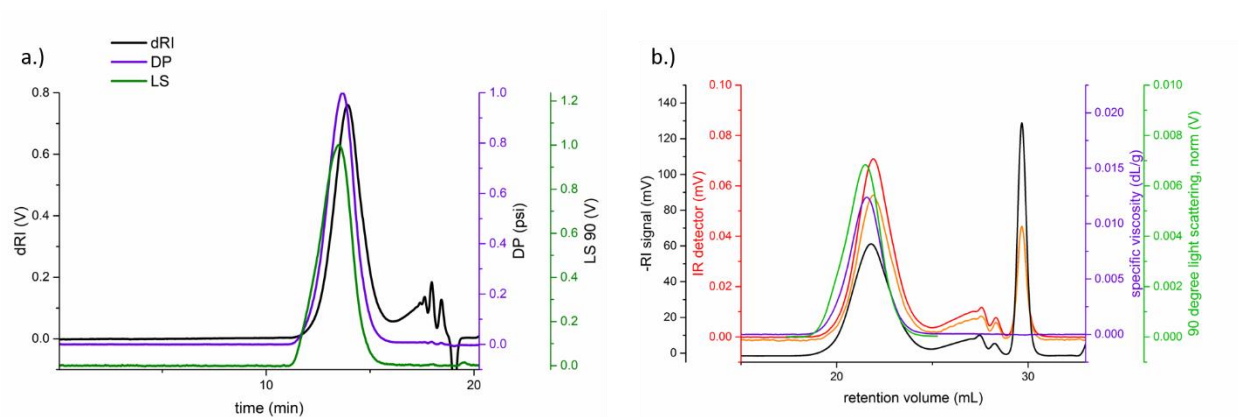


Figure S15. Representative SEC chromatograms for hexyl (C6) branched LLDPE: a) ambient SEC (THF, 35 °C) and b) HT-SEC (TCB, 135 °C). Low molar mass oligomers (broad secondary peak) were estimated to represent $12\% \pm 0.8\%$ of the total concentration, as calculated by HT-SEC RI detection.

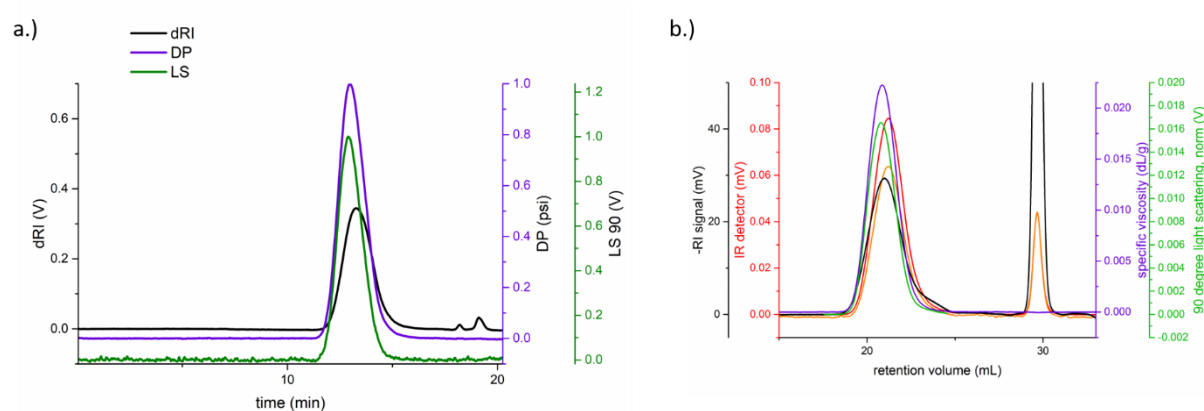


Figure S16. Representative SEC chromatograms for decyl (C10) branched LLDPE: a) ambient SEC (THF, 35 °C) and b) HT-SEC (TCB, 135 °C).

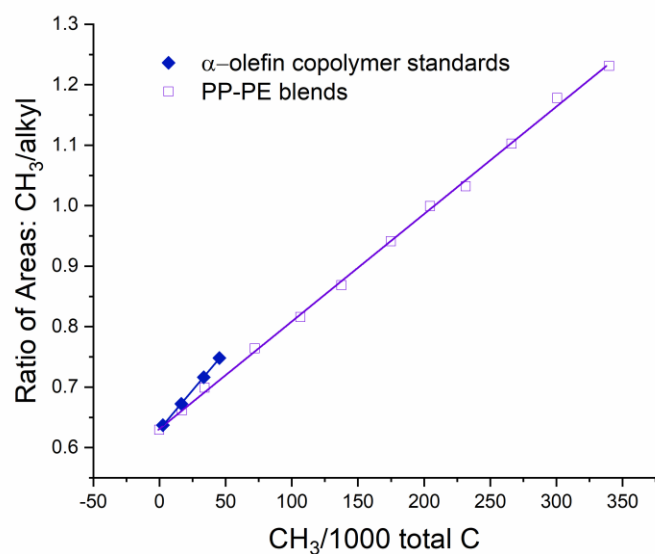


Figure S17. Calibration of IR detector using α -olefin copolymer standards (closed diamonds) and PE-PP blends (open squares)

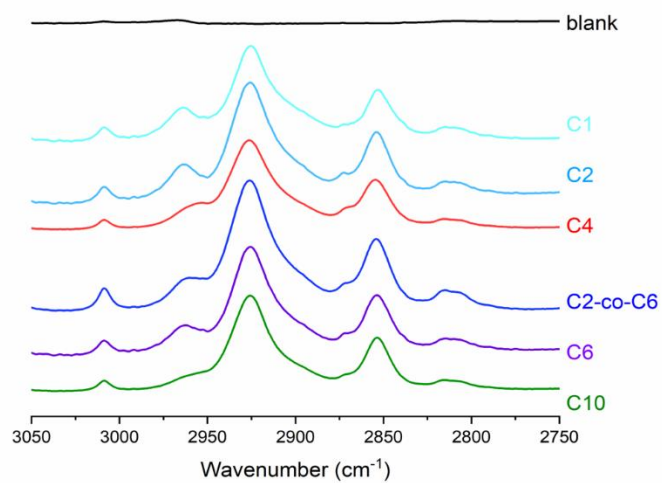


Figure S18. Solution FTIR of LLDPE (TCB, r.t., 5 mg/mL) for all LLDPE studied. The blank is absorbance due to the solvent (TCB) only.

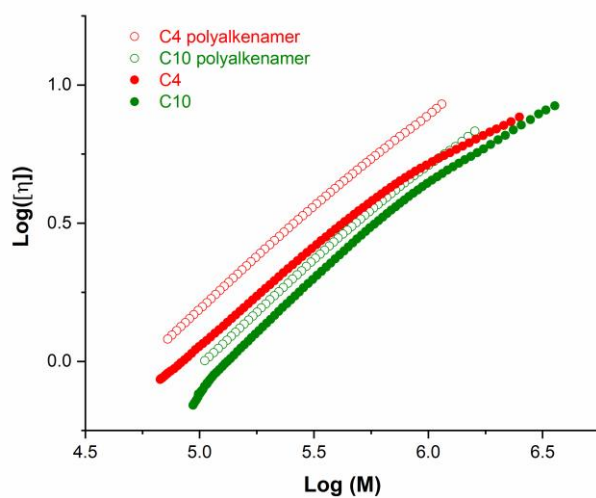


Figure S19. Mark-Houwink plots (HT-SEC, TCB, 135 °C) comparing high molecular mass C4 (red) and C10 (green) polymers pre-hydrogenation (open symbols) and post hydrogenation (filled symbols).

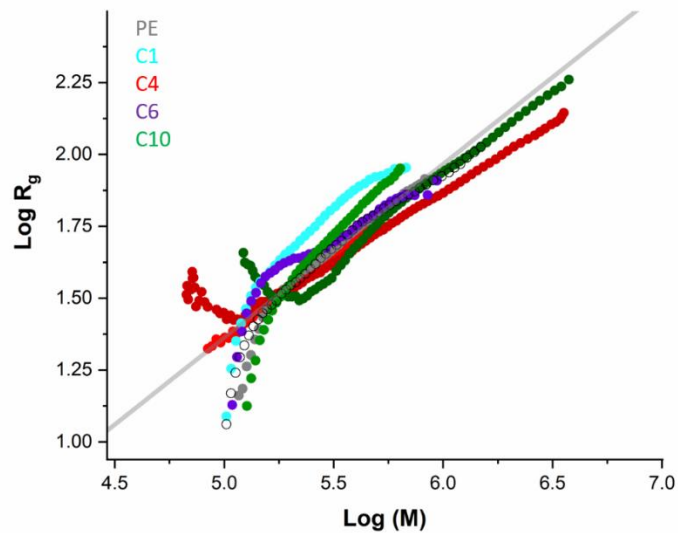


Figure S20. RMS Conformation plot for LLDPEs characterized by HT-SEC (TCB, 135 °C). The open symbols represent the conformation plot of NIST 1475A, linear PE. The grey line represents the linear extrapolation of the standard for clarity.

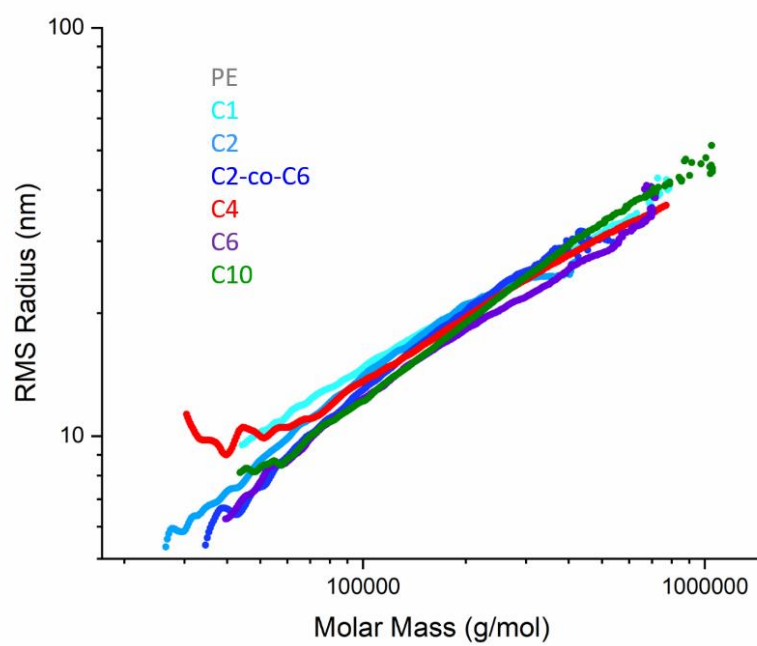


Figure S21. RMS Confirmation plot for LLDPEs characterized by ambient SEC (THF, 35 °C)