

Supplementary information for:

The Aza-Michael reaction: Towards semi-crystalline polymers from renewable itaconic acid and diamines

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Monomer Synthesis

The obtained BPDA monomers are abbreviated to xx-BPDA where xx denotes the type of diamine used: e.g. BPDA with 1,8-octanediamine is abbreviated as C₈-BPDA, BPDA with *trans*-1,4-cyclohexanediamine is abbreviated as *t*-CH-BPDA. The synthesis to obtain BPDA monomers is divided in two synthesis pathways. Either via itaconic acid (**Error! Reference source not found.**, R = H), or via dimethyl itaconate (**Error! Reference source not found.**, R = CH₃) to obtain BPDA monomers with free acid, or dimethyl-ester functionality. The only exception is the synthesis of *p*-Ph-BPDA-dm, which was obtained via methylation of *p*-Ph-BPDA. The monomer synthesis results are shown in **Error! Reference source not found.**, the synthesis details and characterization of novel monomers are described below.

Synthesis of *t*-CH-BPDA

Itaconic acid (9.11 gr, 0.07 mol) and *trans*-1,4-cyclohexanediamine (1.14 gr, 0.01 mol) were loaded in a 100 mL round-bottom flask. The reaction mixture was stirred at 170 °C for 2-6 hours in the melt, or until the reaction mixture was fully solidified. Recrystallization from hot water yielded the product as white solids (2.1 gr, 62% yield). ¹H NMR (CDCl₃, 300 MHz): δ 4.03 (m, 2.06H), 3.82 (m, 3.93 H), 3.48 (p, 2.0H), 3.02 (d, 3.95 H), 1.91 (m, 3.96H), 1.68 (m, 3.90H). ¹³C NMR (CDCl₃, 300 MHz): δ 178.4, 175.2, 162.5, 162.0, 161.4, 160.0, 51.0, 45.9, 35.8, 34.0, 27.7.

Synthesis of *t*-CH-BPDA-dm

Dimethyl itaconate (79.6 gr, 0.5 mol) and *trans*-1,4-cyclohexanediamine (25 gr, 0.22 mmol) were dissolved in 30 mL of methanol in a 250 mL round-bottom flask, equipped with a magnetic stirring bar. The reaction mixture was stirred at reflux overnight, and the product could directly be obtained as white crystals after cooling of the reaction mixture (72.5 gr, 90% yield). ¹H NMR (CDCl₃, 300 MHz): δ 3.97 (m, 2.0H), 3.75 (s, 6.01H), 3.54 (m, 4.38H), 3.22 (p, 2.06H), 2.68 (m, 4.29H), 1.80 (m, 4.22H), 1.59 (m, 4.21H). ¹³C NMR (CDCl₃, 300 MHz): δ 173.2, 172.0, 52.5, 49.4, 44.9, 36.2, 34.6, 28.4.

Synthesis of *c*-CH-BPDA

Itaconic acid (7.8 gr, 60 mmol) and *cis*-1,4-cyclohexanediamine (2.78 gr, 28.8 mmol) were loaded in a 100 mL round-bottom flask. The reaction mixture was stirred at overnight at 130 °C. Recrystallization from boiling water yielded the product as brown solids (yield: n.d.).

Synthesis of *c*-CH-BPDA-dm

Dimethyl itaconate (9.31 gr, 2.18 mmol) and *cis*-1,4-cyclohexanediamine (3.09 gr, 27.05 mmol) were dissolved in 30 mL of methanol in a 100 mL round-bottom flask, equipped with a magnetic stirring bar. The reaction mixture was stirred at reflux overnight to yield a viscous orange oil. The product was isolated after column chromatography (MeOH:CHCl₃ 1:19v%, RF 0.48) as a yellow oil. (5.73 gr, 63% yield). ¹H NMR (CDCl₃, 300 MHz): δ 3.96 (m, 2.0H), 3.69 (s, 6.0H), 3.65 (m, 3.84H), 3.16 (p, 2.0H), 2.63 (d, 3.98H), 1.82 (m, 3.95H), 1.64 (m, 4.16H). ¹³C NMR (CDCl₃, 300 MHz): δ 173.3, 172.3, 52.5, 48.1, 47.3, 36.4, 34.5, 30.0.

Synthesis of *t*-CP-BPDA

Itaconic acid (2.71 gr, 20.9 mmol) and *trans*-1,3-cyclopentanediamine (0.97 gr, 9.65 mmol) were loaded in a 100 mL round-bottom flask. The reaction mixture was stirred overnight at 130 °C. Recrystallization from boiling water yielded the product as white solids (2.74 gr, 88% yield).

Synthesis of *t*-CP-BPDA-dm

Dimethyl itaconate (8.98 gr, 56.8 mmol) and *trans*-1,3-cyclopentanediamine (2.74 gr, 27.4 mmol) were dissolved in 30 mL of methanol in a 100 mL round-bottom flask, equipped with a magnetic stirring bar. The reaction mixture was stirred at reflux overnight to yield a viscous orange oil. The product was isolated after column chromatography MeOH:CHCl₃ 3:97v%) as a yellow oil. (5.12 gr, 53 yield). ¹H NMR (CDCl₃, 300 MHz): δ 3.97 (m 2.0H), 3.75 (s, 6.01H), 3.54 (m, 4.38H), 3.22 (p, 2.06H), 2.68 (m, 4.29H), 1.80 (4.22H), 1.59 (m, 4.21H). ¹³C NMR (CDCl₃, 300 MHz): δ

Synthesis of *c*-CP-BPDA

Itaconic acid (2.57 gr, 19.8 mmol) and *cis*-1,3-cyclopentanediamine (0.98 gr, 9.77 mmol) were loaded in a 100 mL round-bottom flask. The reaction mixture was stirred overnight at 130 °C. Recrystallization from boiling water yielded the product as white solids (2.85 gr, 90% yield).

Synthesis of *c*-CP-BPDA-dm

Dimethyl itaconate (9.84 gr, 60 mmol) and *cis*-1,3-cyclopentanediamine (2.87, 28.7 mmol) were dissolved in 30 mL of methanol in a 100 mL round-bottom flask, equipped with a magnetic stirring bar. The reaction mixture was stirred at reflux overnight to yield a viscous orange oil. The product was isolated after column chromatography (MeOH:CHCl₃ 3:97v%) as a yellow oil. (5.59 gr, 55 yield). ¹H NMR (CDCl₃, 300 MHz): δ 4.66 (p, 1.86H), 3.75 (s, 6.0H), 3.60 (d, 3.95H), 3.23 (p, 1.97H), 2.70 (m, 4.0H), 2.0 (1.90H), 1.86 (m, 2.60H), 1.61 (m, 1.78H). ¹³C NMR (CDCl₃, 300 MHz): δ 173.2, 172.2, 52.5, 50.8, 45.5, 36.1, 34.7, 31.0, 26.9.

Synthesis of *p*-Ph-BPDA

Itaconic acid (7.83 gr, 60.2 mmol) and *para*-phenylenediamine (3.25 gr, 30.1 mmol) were loaded in a 100 mL round-bottom flask. The reaction mixture was stirred overnight at 130 °C. Recrystallization from boiling water yielded the product as white solids (11.5 gr, 99% yield). ¹H NMR (CDCl₃, 300 MHz): δ 7.55 (s, 4.0H), 4.26 (m, 4.04H), 3.60 (p, 2.09H), 3.20 (d, 4.0H). ¹³C NMR (CDCl₃, 300 MHz): δ 178.3, 162.5, 161.9, 161.3, 160.7, 135.4, 123.4, 51.7, 35.7, 34.6.

Synthesis of *p*-Ph-BPDA-dm

P-Ph-BPDA (5.1 gr, 15.3 mmol) was suspended in 100 mL of methanol with 2 mL of sulfuric acid in a 250 mL round-bottom flask. The suspension was refluxed for 72 hours, the methanol and formed water were removed *in vacuo*, the obtained product was re-suspended in 100 mL of methanol and refluxed for another 18 hr. The suspension was a grey slurry in deep purple liquid. After cooling, the product could be isolated as a grey solid by filtration (4.45 gr, 81% yield). ¹H NMR (CDCl₃, 300 MHz): δ 7.54 (s, 4.0H), 3.99 (m, 4.15H), 3.72 (s, 5.97H), 3.31 (p, 2.16H), 2.84 (m, 4.19H).

Synthesis of *m*-Xy-BPDA-dm

Dimethyl itaconate (20.7 gr, 130.9 mmol) and *meta*-xylylenediamine (8.7 gr, 63.9 mmol) were dissolved in 30 mL of methanol in a 100 mL round-bottom flask, equipped with a magnetic stirring bar. The reaction mixture was stirred at reflux overnight to yield a viscous orange oil. The product was isolated after column chromatography (MeOH:CHCl₃ 7:93v%) as a yellow oil (yield 77%).

Synthesis of *p*-Xy-BPDA

Itaconic acid (7.22 gr, 55.5 mmol) and *para*-xylylenediamine (3.78 gr, 27.7 mmol) were loaded in a 100 mL round-bottom flask. The reaction mixture was stirred overnight at 130 °C. Recrystallization from boiling water yielded the product as white solids (yield n.d.).

Synthesis of *p*-Xy-BPDA-dm

Dimethyl itaconate (20.4 gr, 128.7 mmol) and *para*-xylylenediamine (8.8 gr, 61.3 mmol) were dissolved in 30 mL of methanol in a 100 mL round-bottom flask, equipped with a magnetic stirring bar. The reaction mixture was stirred at reflux overnight, and the product could directly be obtained as white crystals after cooling of the reaction mixture (17.5 gr, 74% yield). ¹H NMR (CDCl₃, 300 MHz): δ 7.22 (2, 4.0H), 4.45 (m, 4.07H), 3.73 (s, 6.0H), 3.48 (m, 3.83H), 3.23 (p, 2.03H), 2.76 (m, 4.08H).

NMR analysis of monomers

NMR analysis of *t*-CP-BPDA-dm

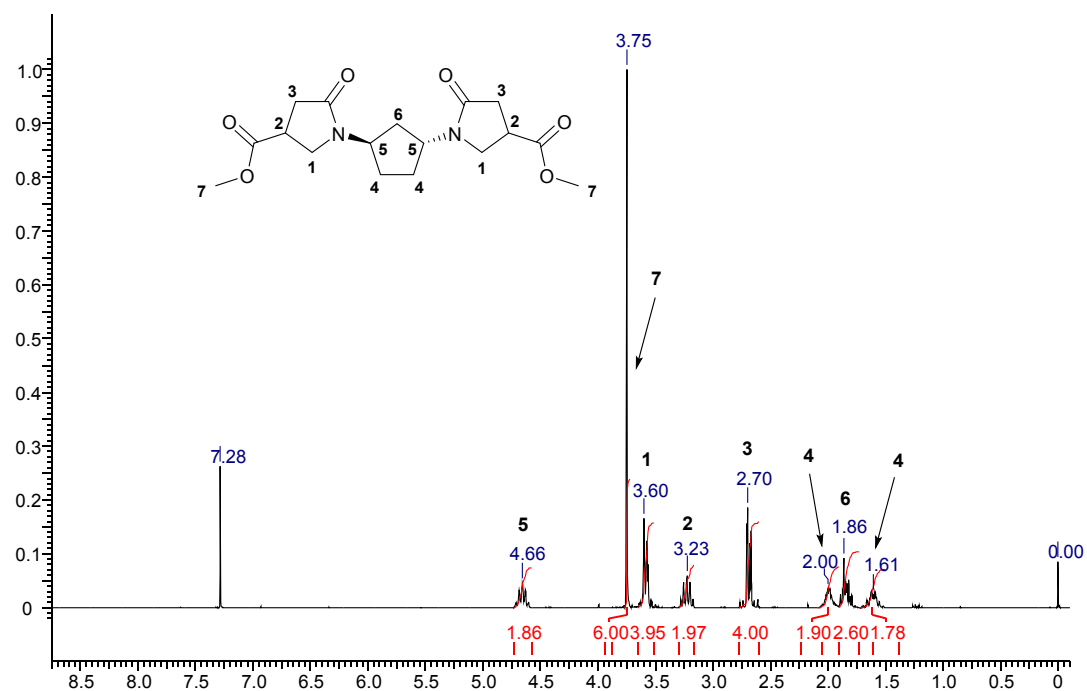


Figure 1. ¹H-NMR of *t*-CP-BPDA-dm.

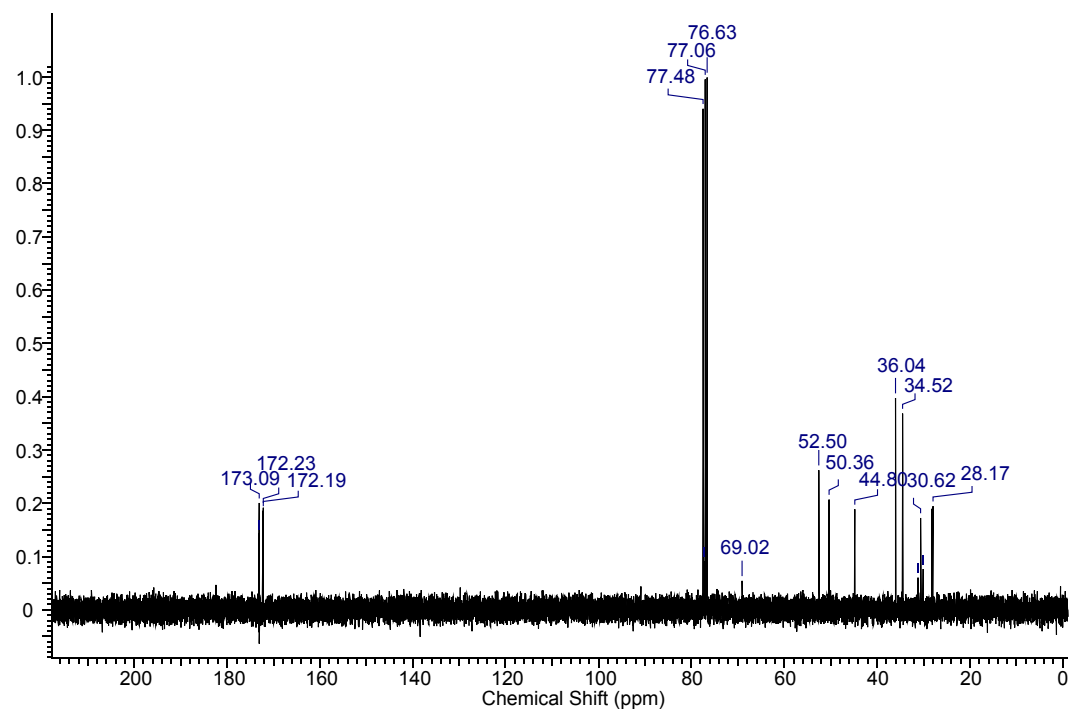


Figure 2. ¹³C-NMR of *t*-CP-BPDA-dm.

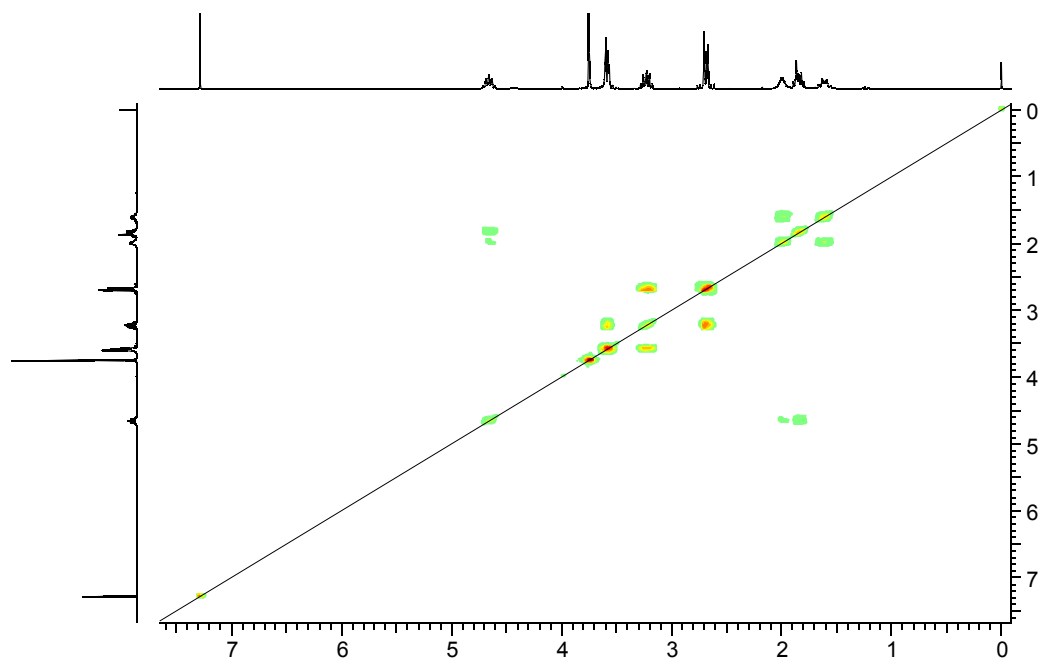


Figure 3. COSY (^1H - ^1H) NMR of *t*-CP-BPDA-dm.

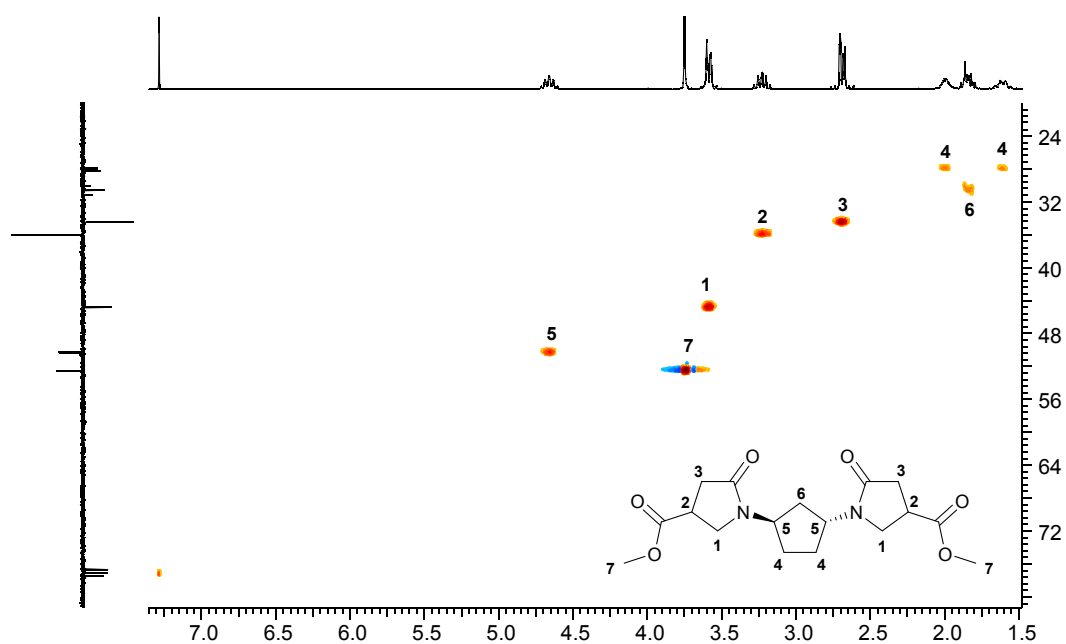


Figure 4. HSQC (^1H - ^{13}C APT) NMR of *t*-CP-BPDA-dm.

NMR analysis of *c*-CP-BPDA-dm

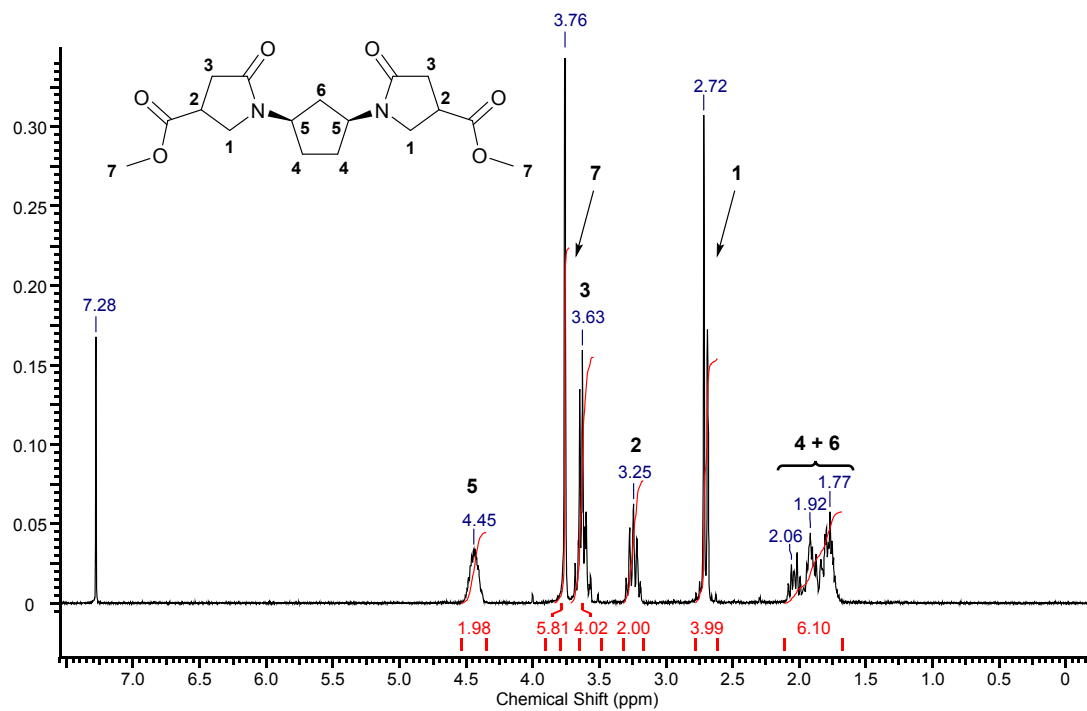


Figure 5. ¹H-NMR of *c*-CP-BPDA-dm.

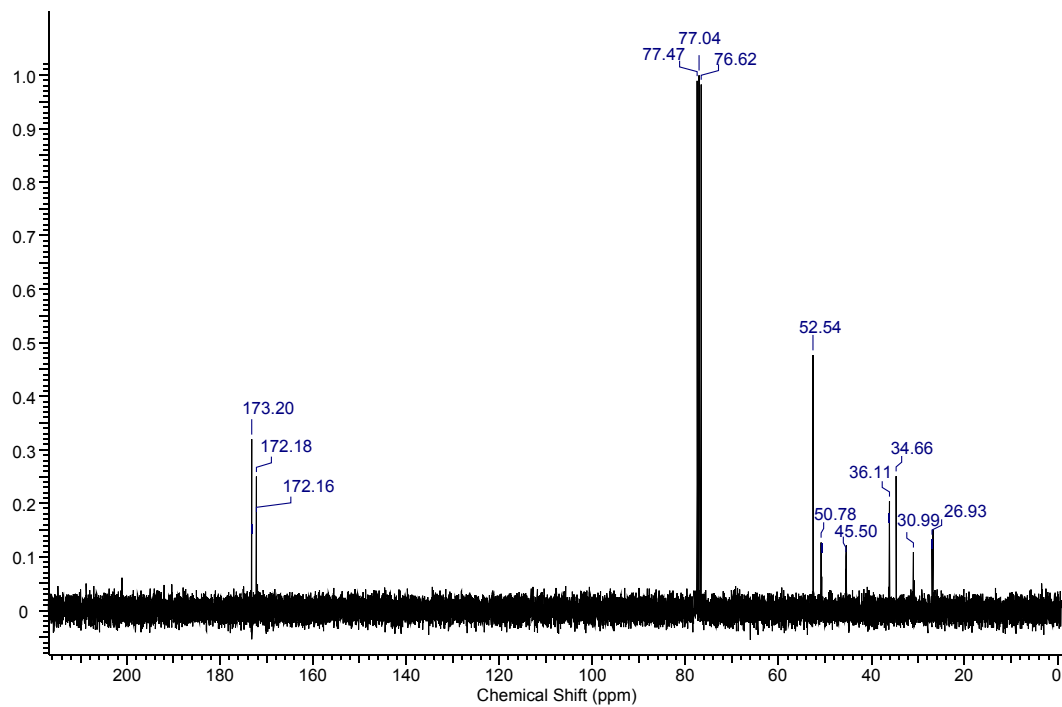


Figure 6. ¹³C-NMR of *c*-CP-BPDA-dm.

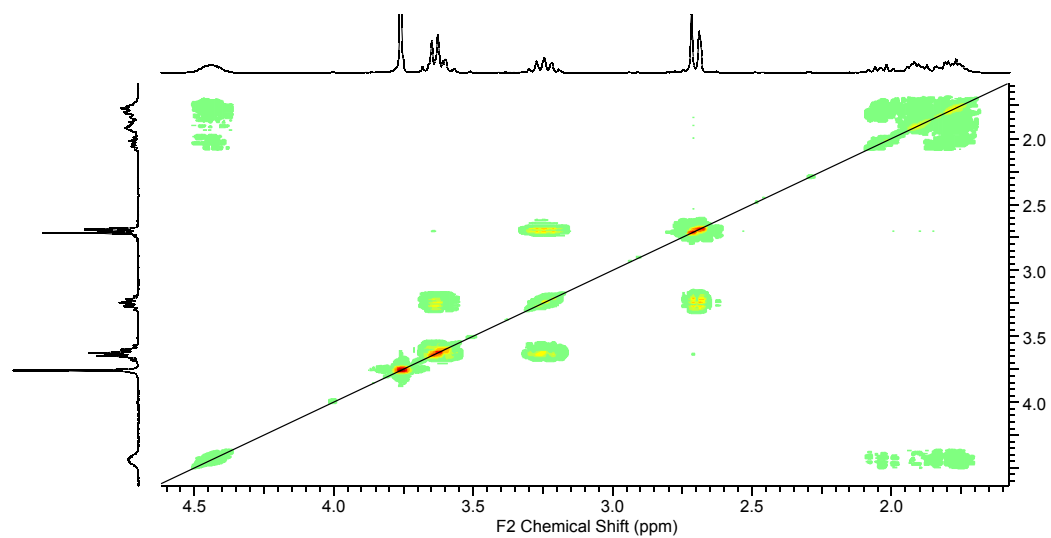


Figure 7. COSY (^1H - ^1H) NMR of *c*-CP-BPDA-*dm*.

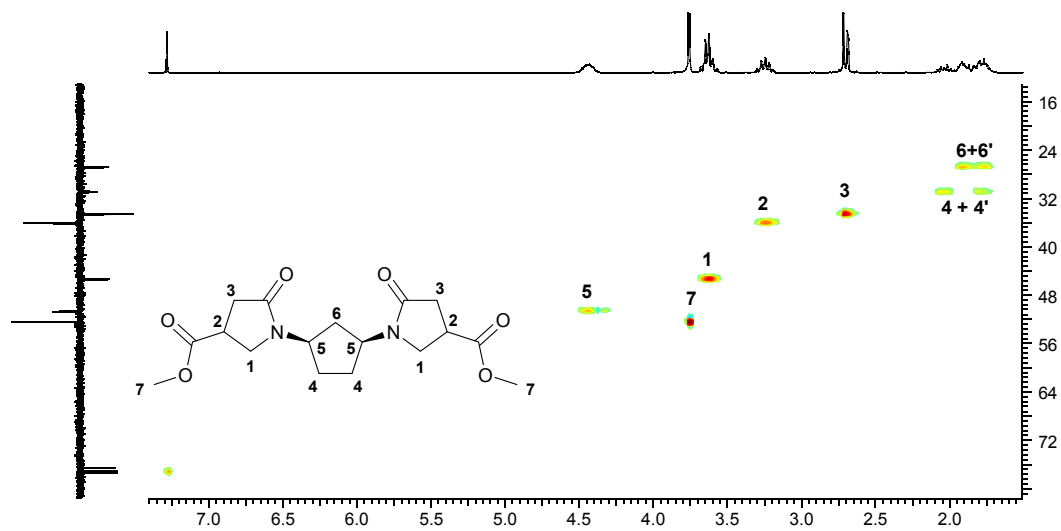


Figure 8. HSQC (^1H - ^{13}C APT) NMR of *c*-CP-BPDA-*dm*.

NMR analysis of *t*-CH-BPDA-dm

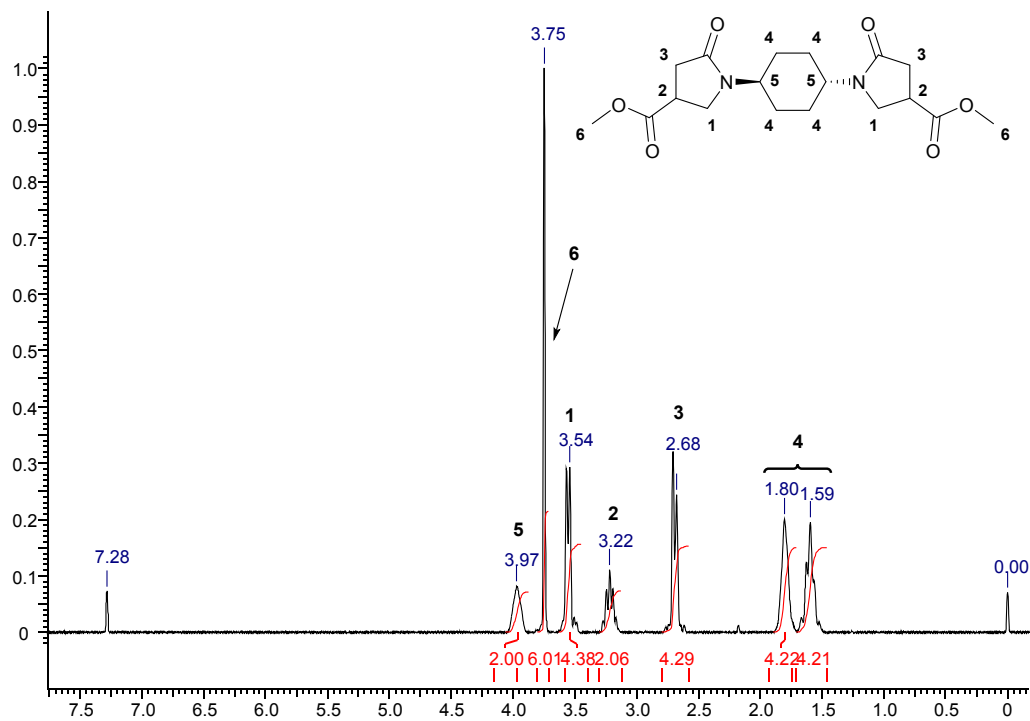


Figure 9. ¹H-NMR of *t*-CH-BPDA-dm.

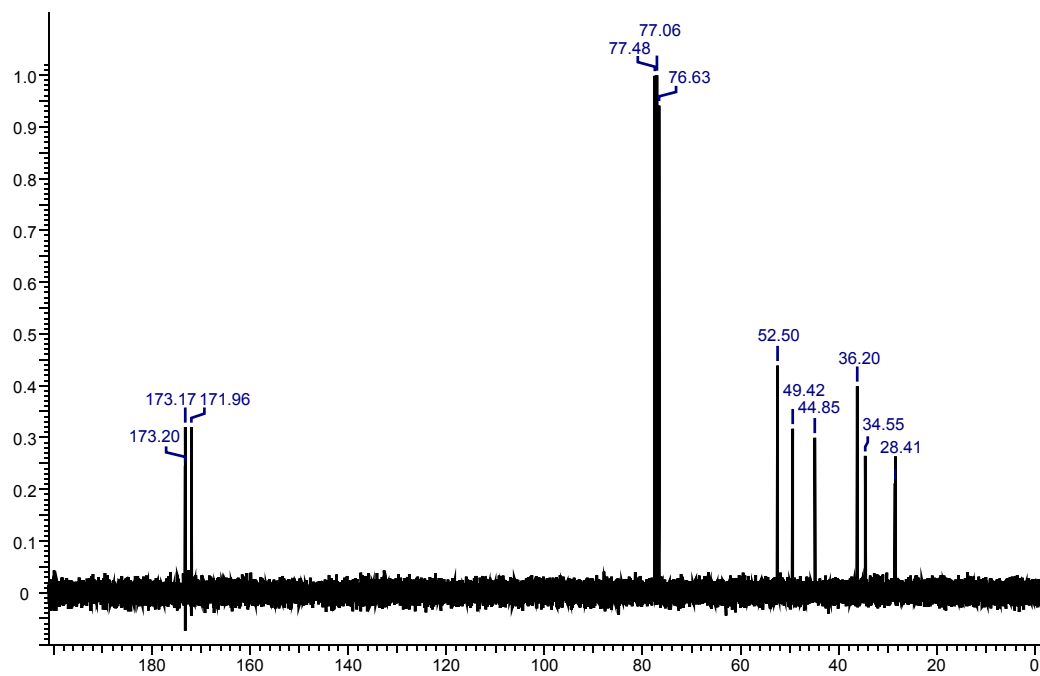


Figure 10. ¹³C-NMR of *t*-CH-BPDA-dm.

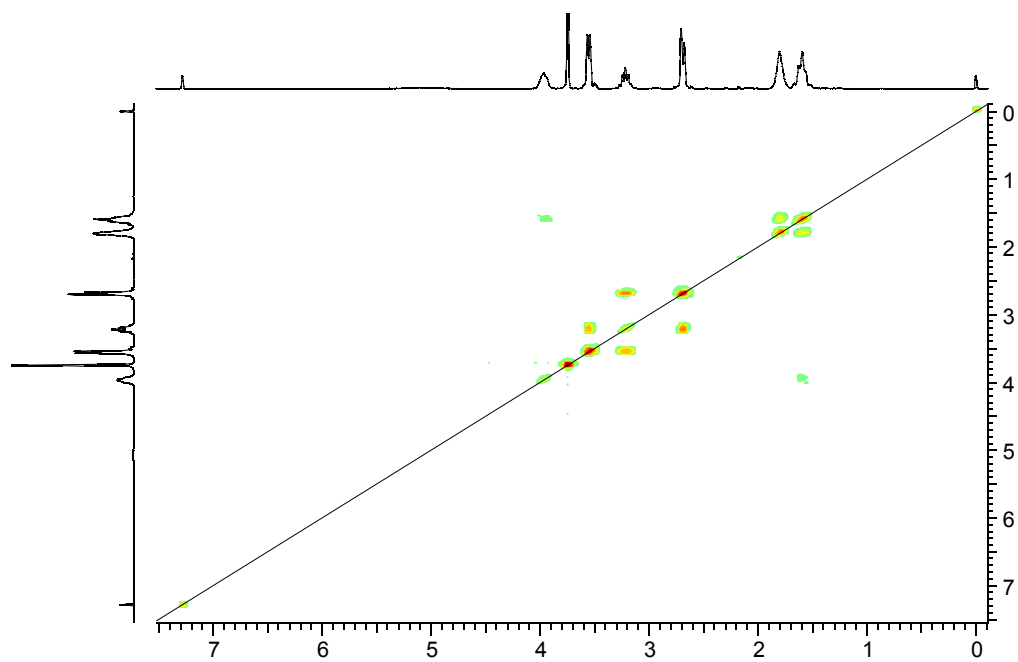


Figure 11. COSY (^1H - ^1H) NMR of *t*-CH-BPDA-dm.

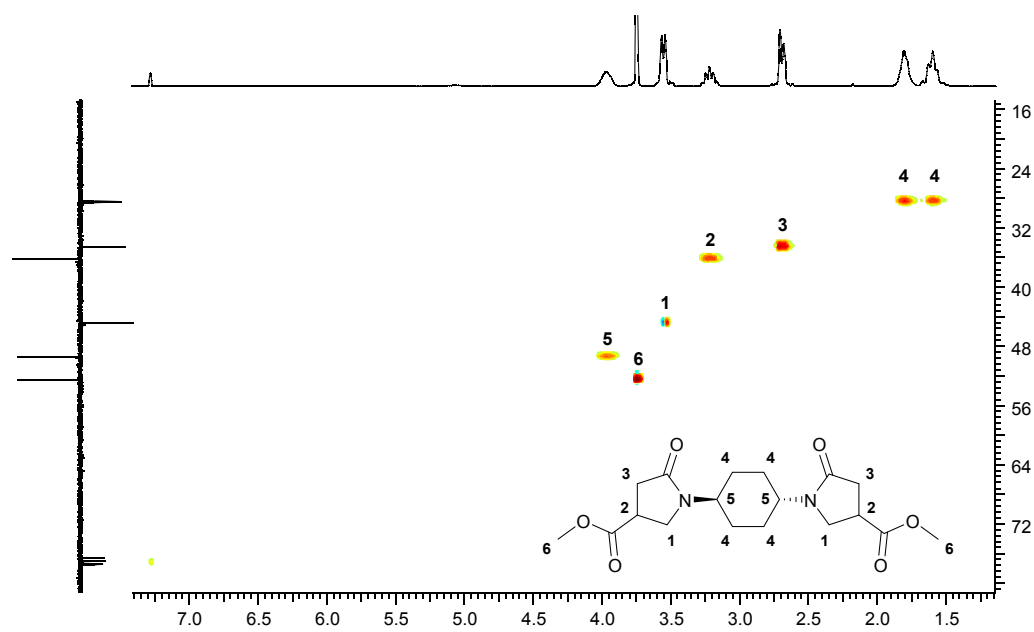


Figure 12. HSQC (^1H - ^{13}C APT) NMR of *t*-CH-BPDA-dm.

NMR analysis of *t*-CH-BPDA

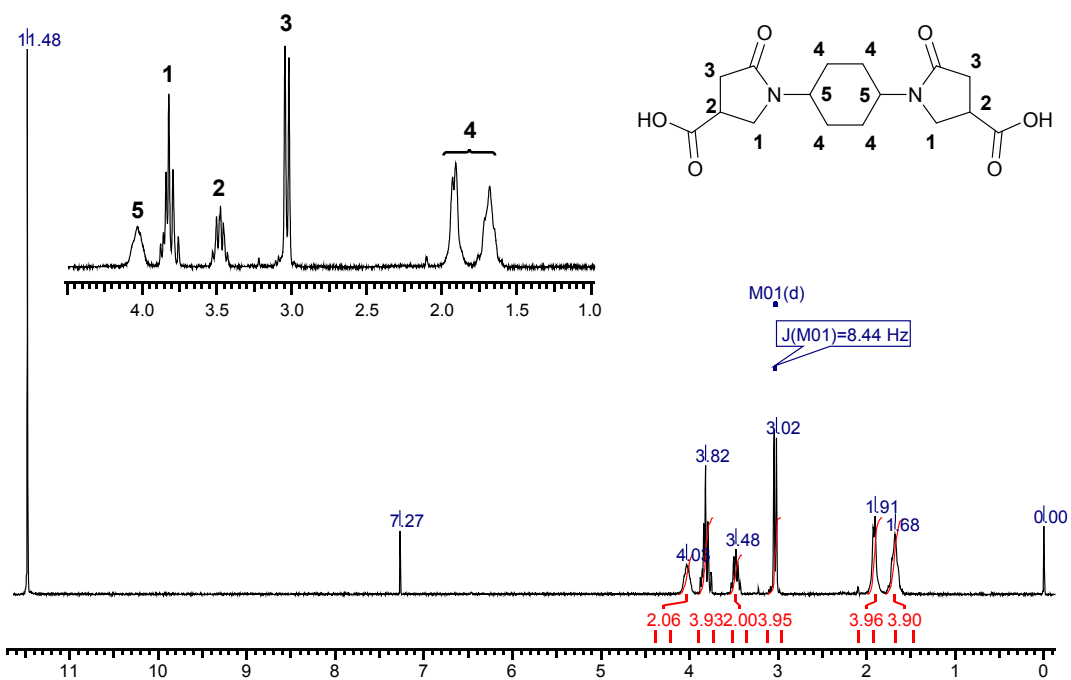


Figure 13. ¹H-NMR of *t*-CH-BPDA.

NMR analysis of *c*-CH-BPDA-dm

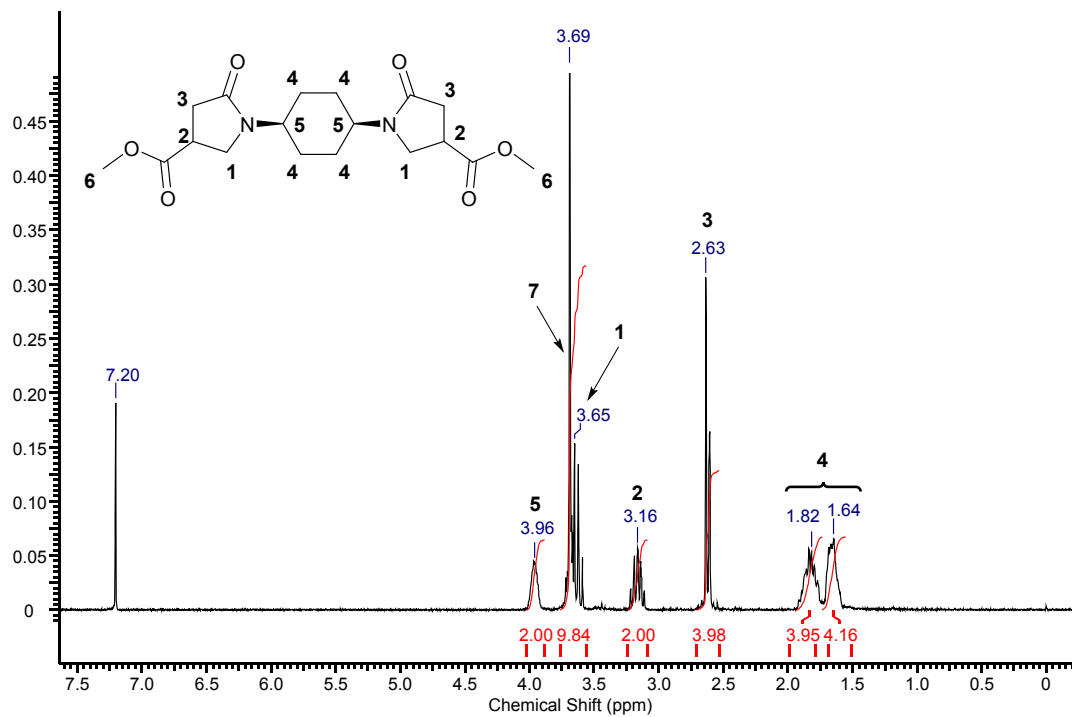


Figure 14. ¹H-NMR of *c*-CH-BPDA-dm.

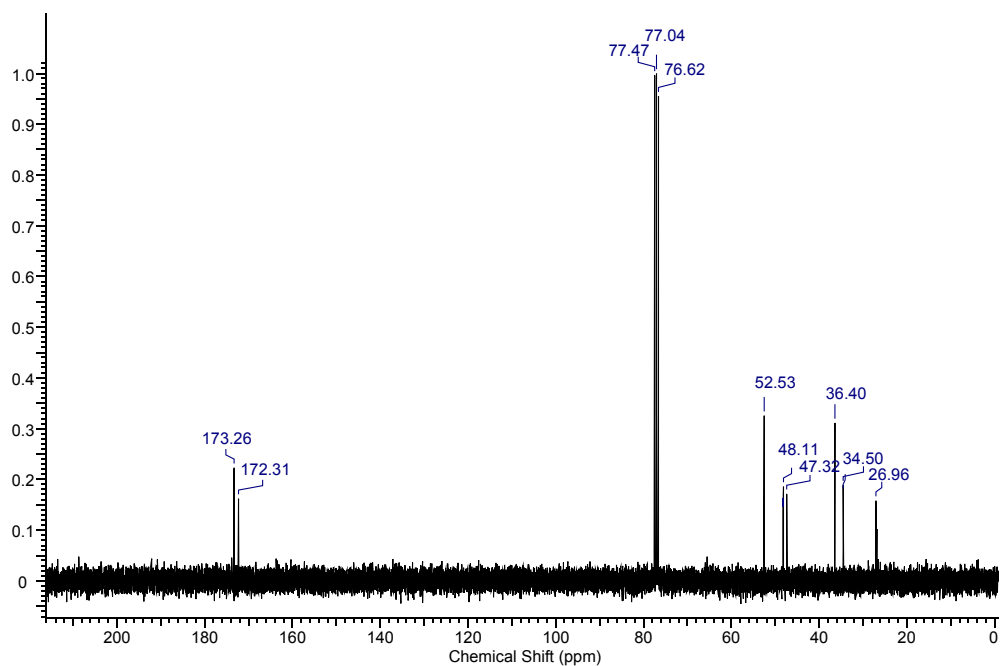


Figure 15. ^{13}C -NMR of *c*-CH-BPDA-dm.

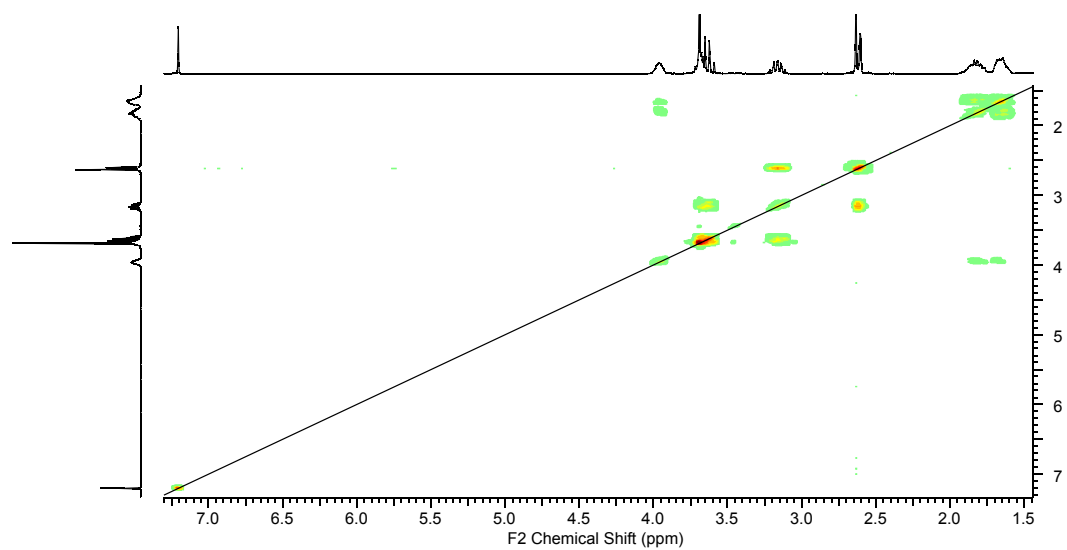


Figure 16. COSY (^1H - ^1H) NMR of *c*-CH-BPDA-dm.

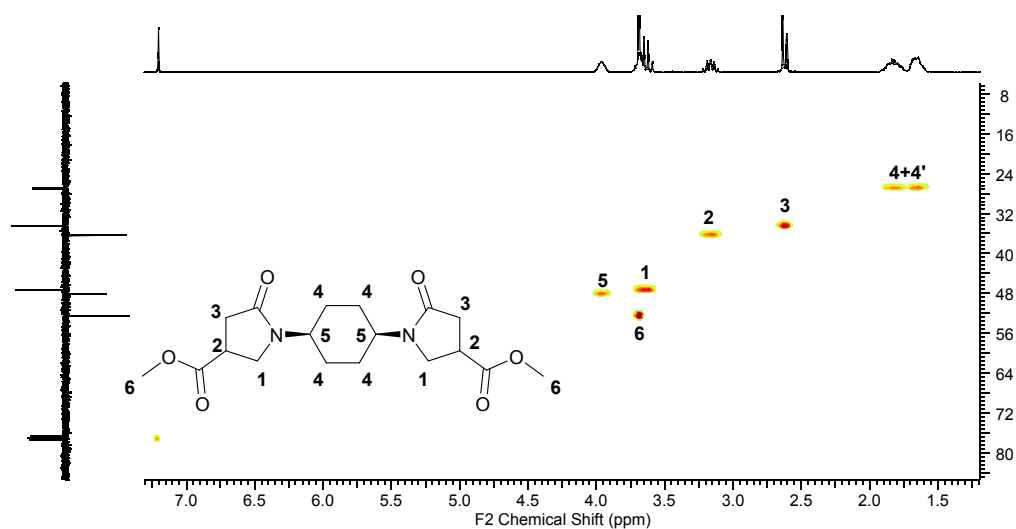


Figure 17. HSQC (^1H - ^{13}C APT) NMR of *c*-CH-BPDA-dm.

NMR analysis of *p*-Ph-BPDA-dm

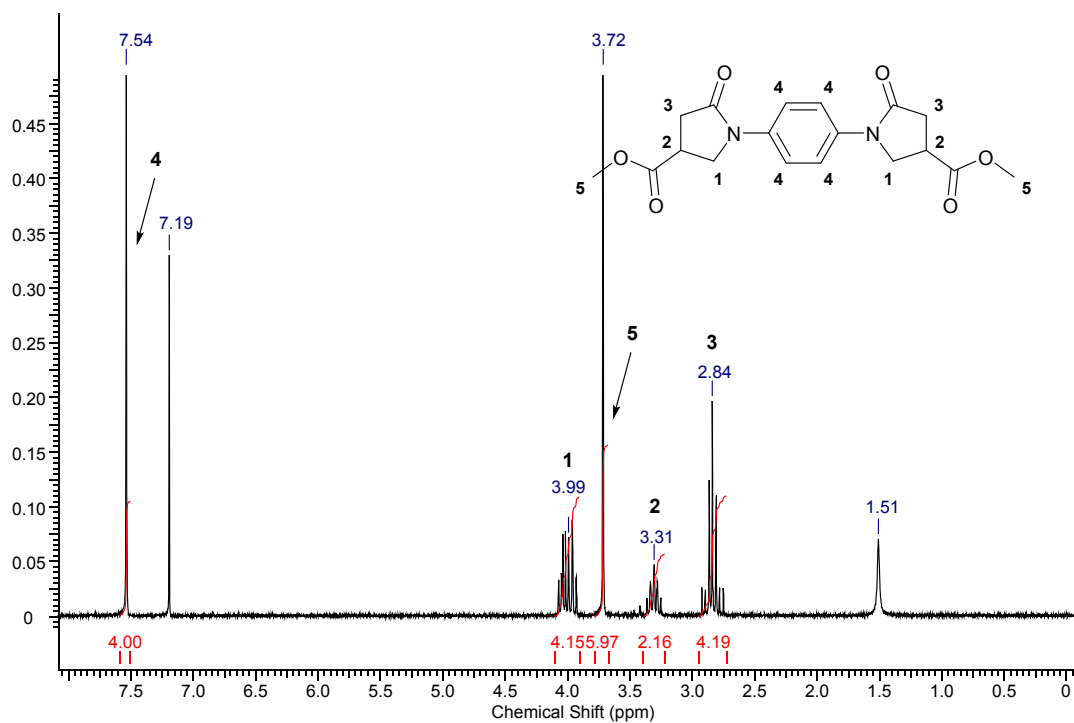


Figure 18. ^1H -NMR of *p*-Ph-BPDA-dm.

NMR analysis of *p*-Ph-BPDA

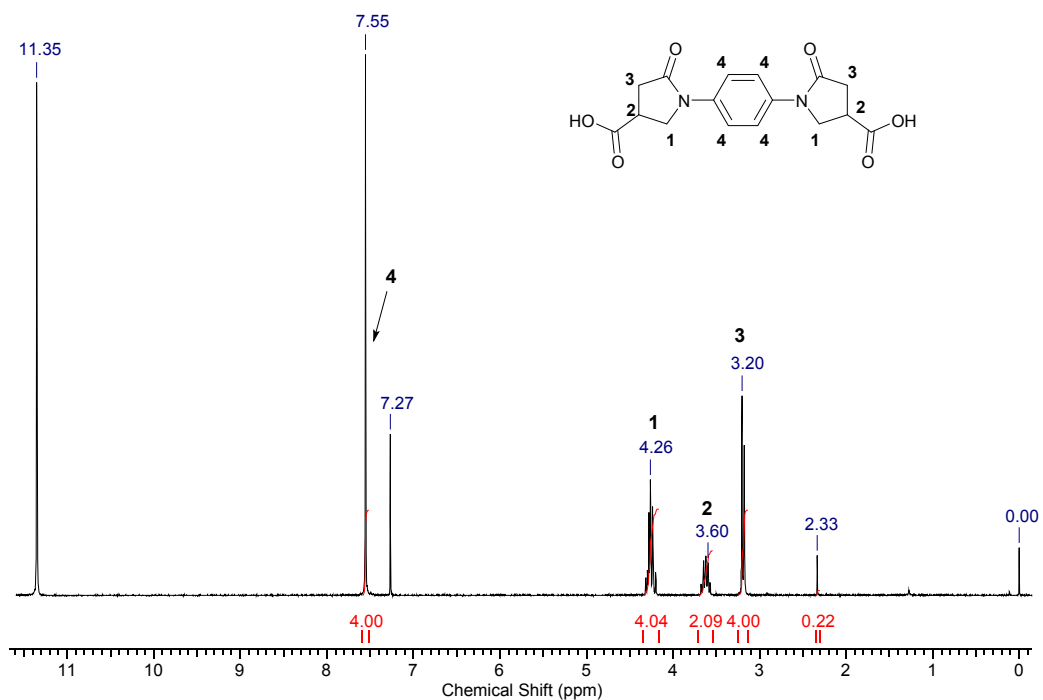


Figure 19. ¹H-NMR of *p*-Ph-BPDA.

NMR analysis of *p*-Xy-BPDA-dm

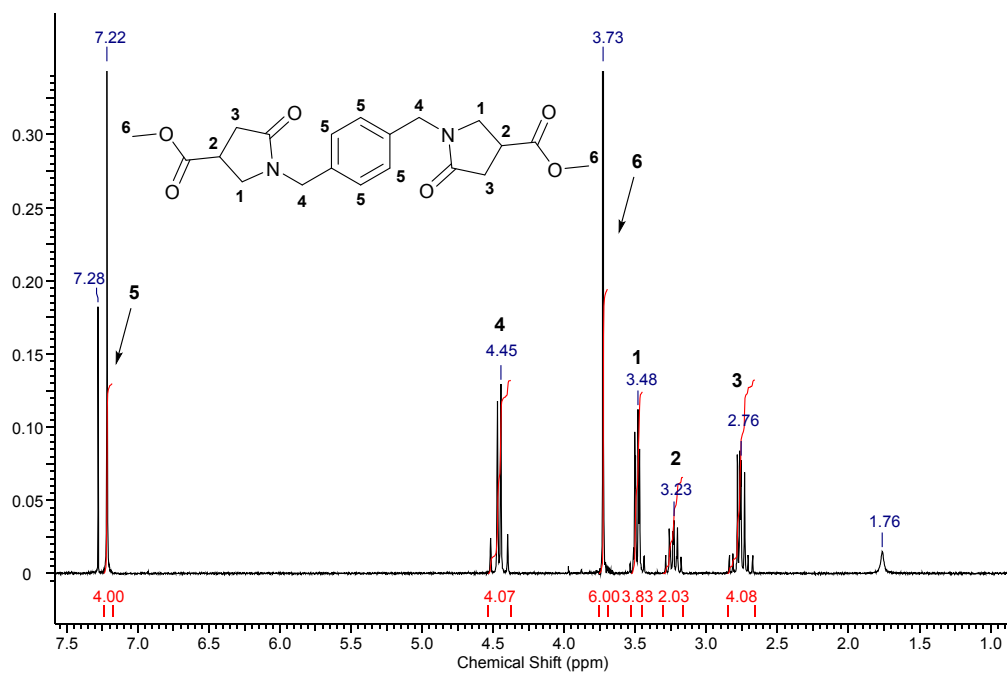


Figure 20. ¹H-NMR of *p*-Xy-BPDA-dm.

TGA analysis of monomers

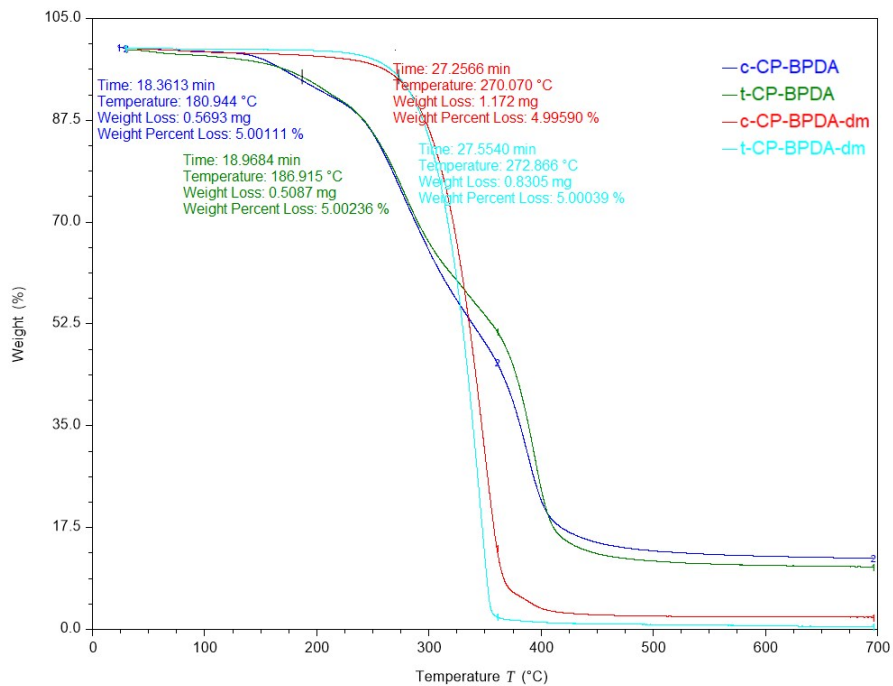


Figure 21. TGA of monomers c-CP-BPDA (light blue), c-CP-BPDA-dm (green), t-CP-BPDA (red), t-CP-BPDA-dm (blue).

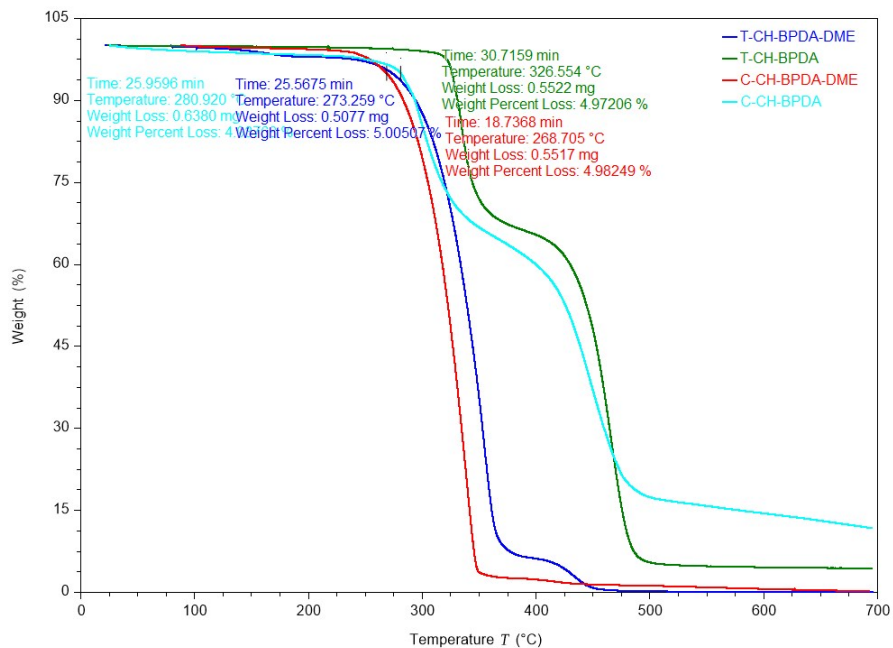


Figure 22. TGA of monomers c-CH-BPDA (light blue), c-CH-BPDA-dm (red), t-CH-BPDA (green), t-CH-BPDA-dm (blue).

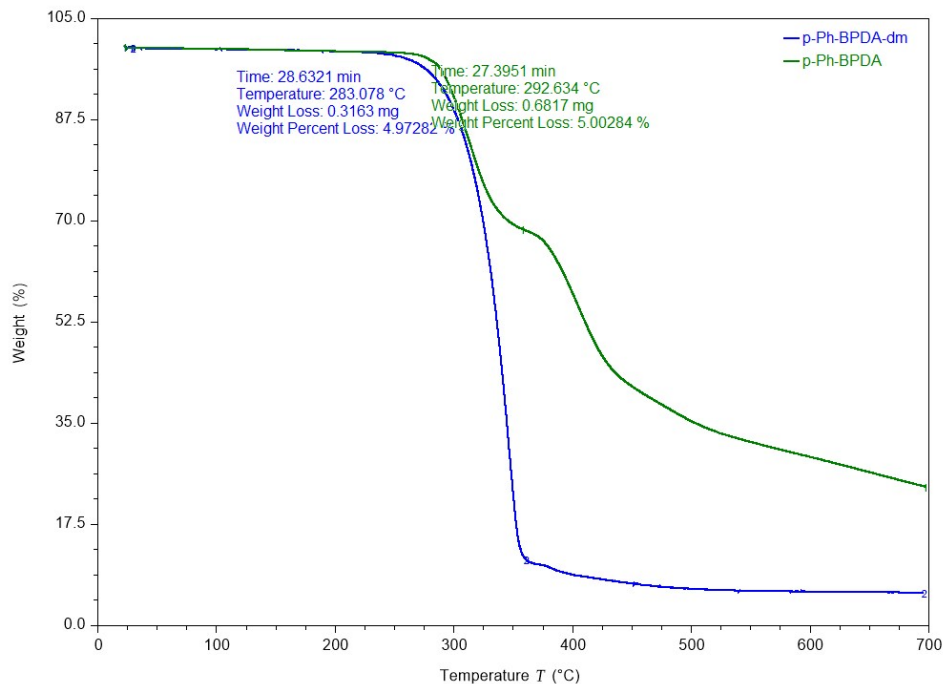


Figure 23. TGA of monomers *p*-Ph-BPDA (green) and *p*-Ph-BPDA-dm.

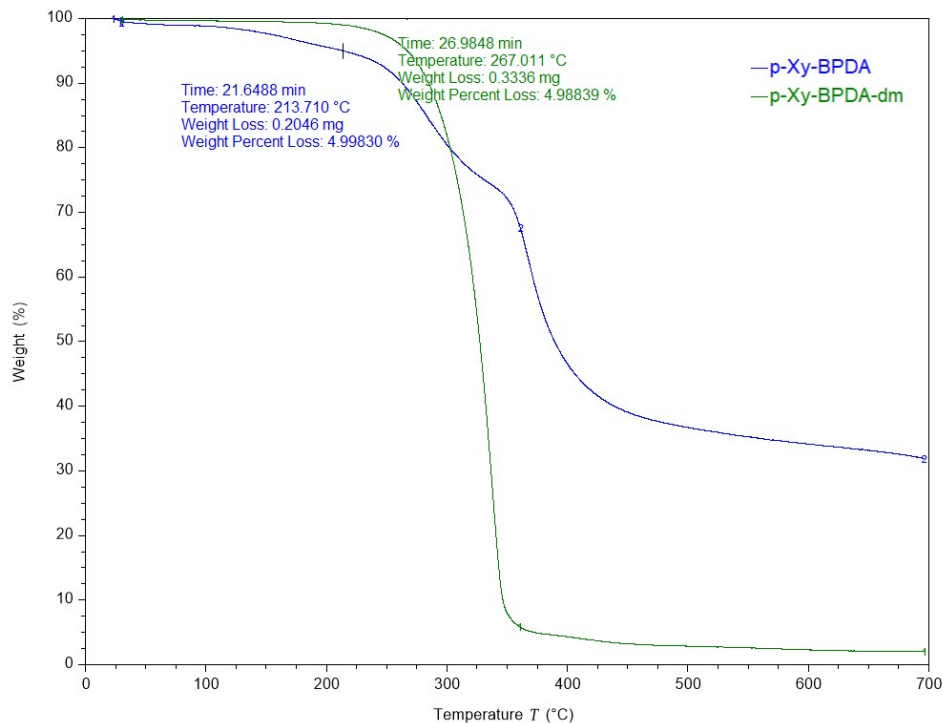


Figure 24. TGA of monomers *p*-Xy-BPDA (blue) and *p*-Xy-BPDA-dm (green).

NMR analysis of organic BPDA-diamine salts

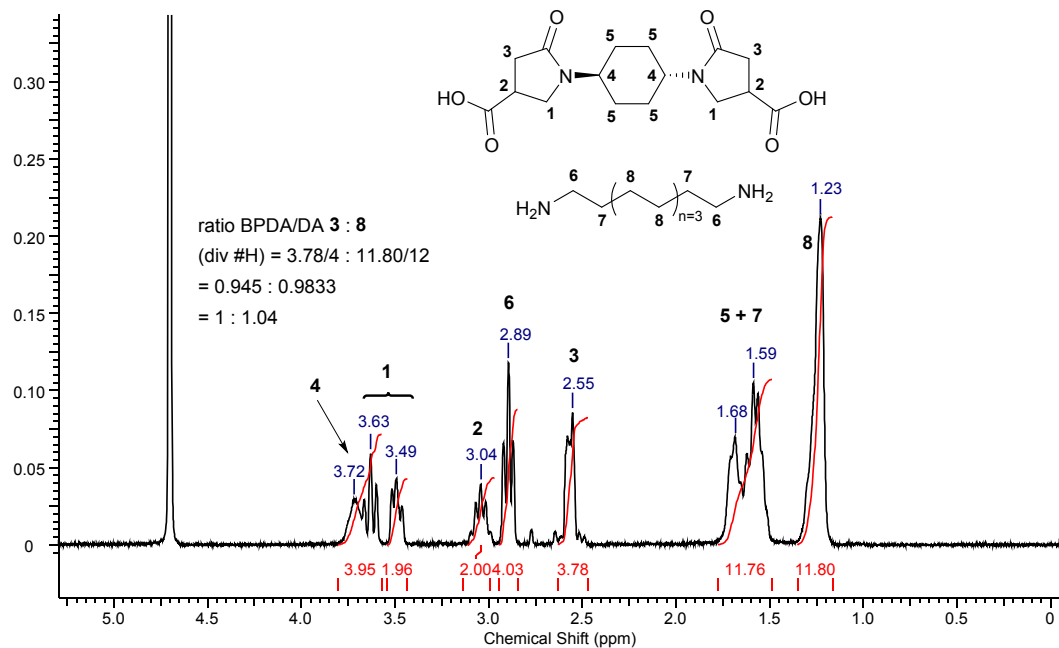


Figure 25. ¹H-NMR analysis of organic salt of t-CH-BPDA and 1,10-decanediamine.

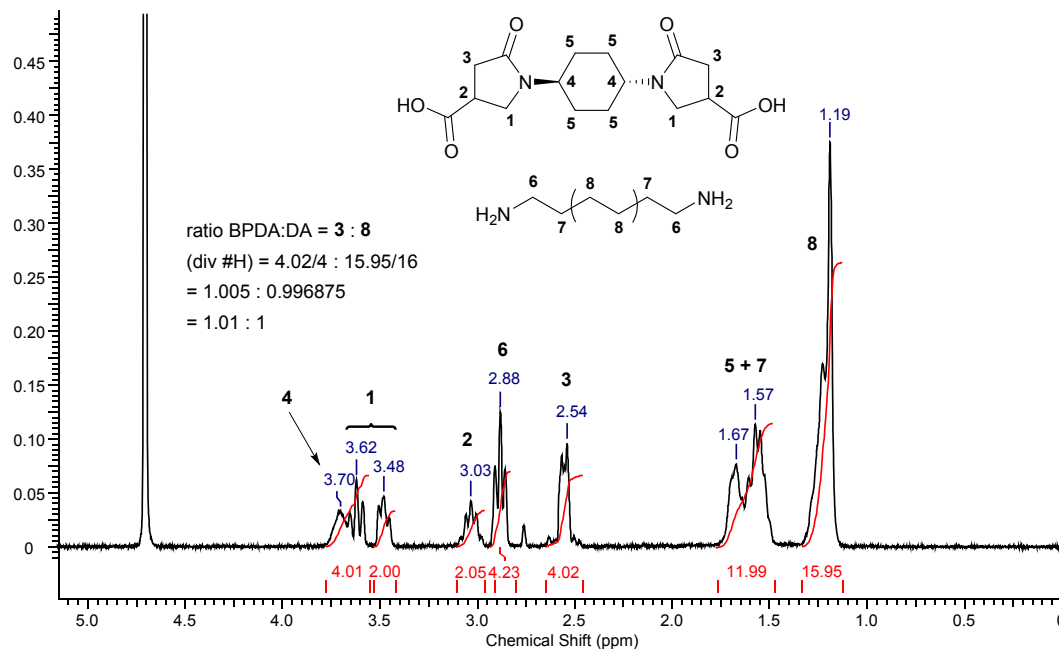


Figure 26. ¹H-NMR analysis of organic salt of t-CH-BPDA and 1,12-dodecanediamine.

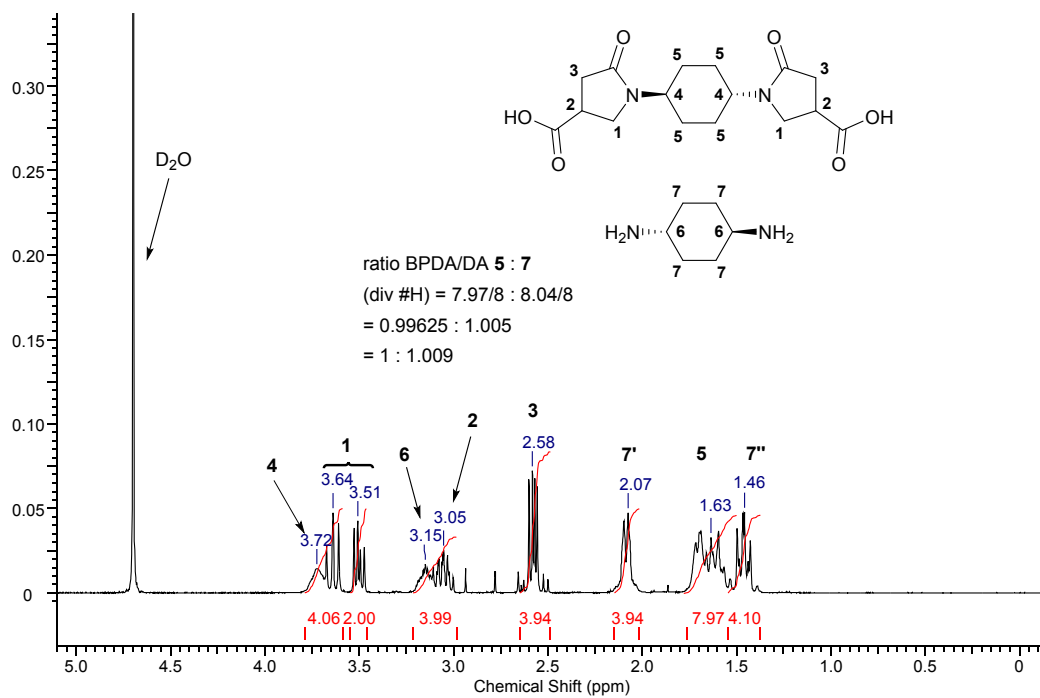


Figure 27. $^1\text{H-NMR}$ analysis of organic salt of *t*-CH-BPDA and *t*-CHdiamine.

TGA analysis of organic BPDA-diamine salts

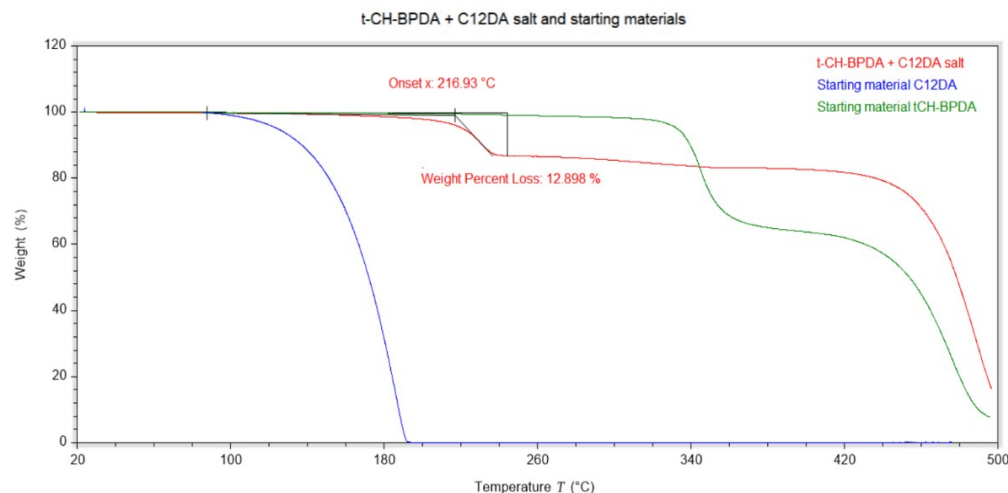


Figure 28. TGA analysis of starting materials 1,12-dodecanediamine (blue), *t*-CH-BPDA (green), and the organic salt of *t*-CH-BPDA with 1,12-dodecanediamine (red). Visible is the evaporation of 1,12-dodecanediamine above 100 °C, thermal decarboxylation of *t*-CH-BPDA above 320 °C, and the change in thermal stability of the organic salt when heated.

TGA analysis of BPDA-based polyamides

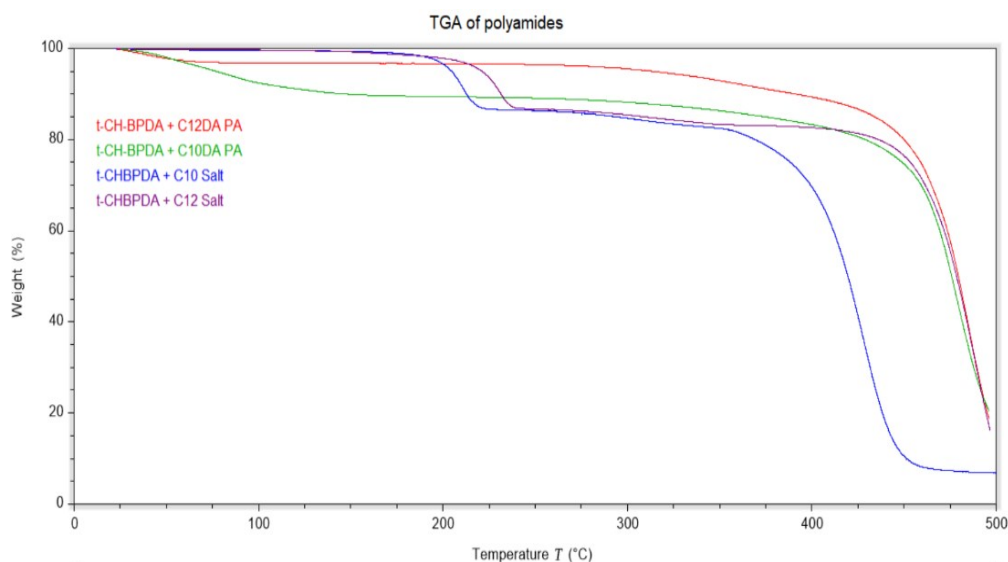


Figure 29. TGA analysis of organic salt of *t*-CH-BPDA with 1,10-decanediamine (blue), and the organic salt of *t*-CH-BPDA with 1,12-dodecanediamine (purple), and the corresponding polyamides (green, and red, respectively).

NMR analysis of BPDA-based polyesters

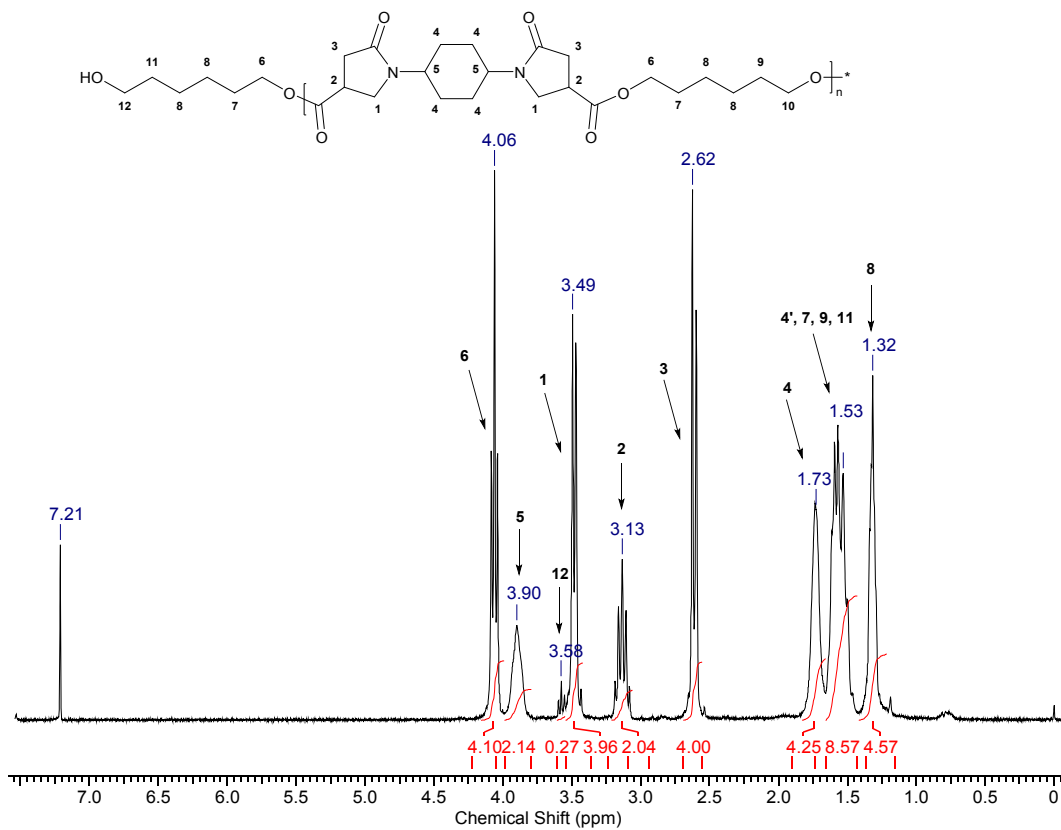


Figure 30. ¹H NMR analysis of poly([t-CH-BPDA]-C₆).

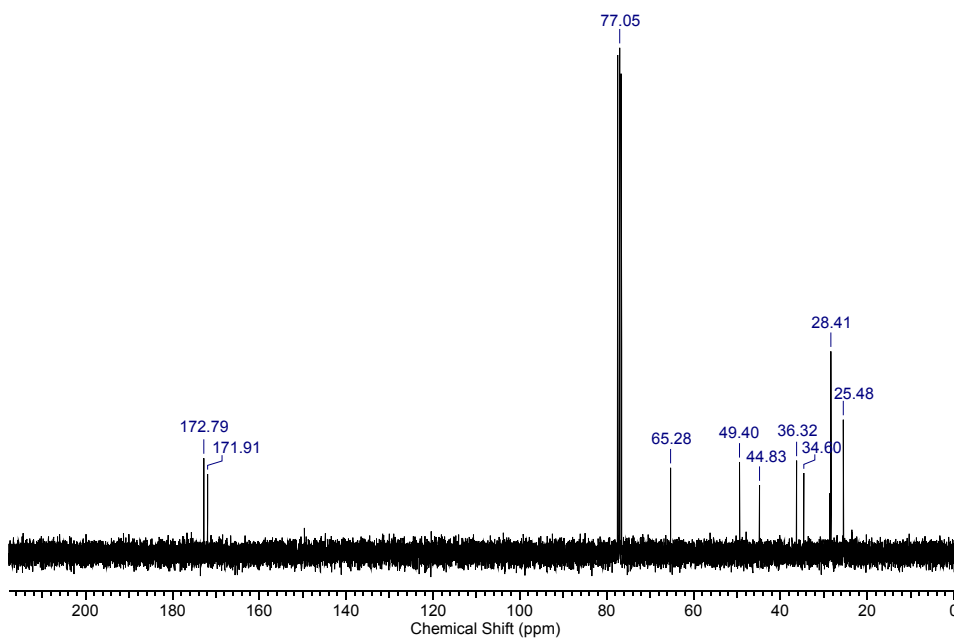


Figure 31. ¹³C NMR analysis of poly([t-CH-BPDA]-C₆).

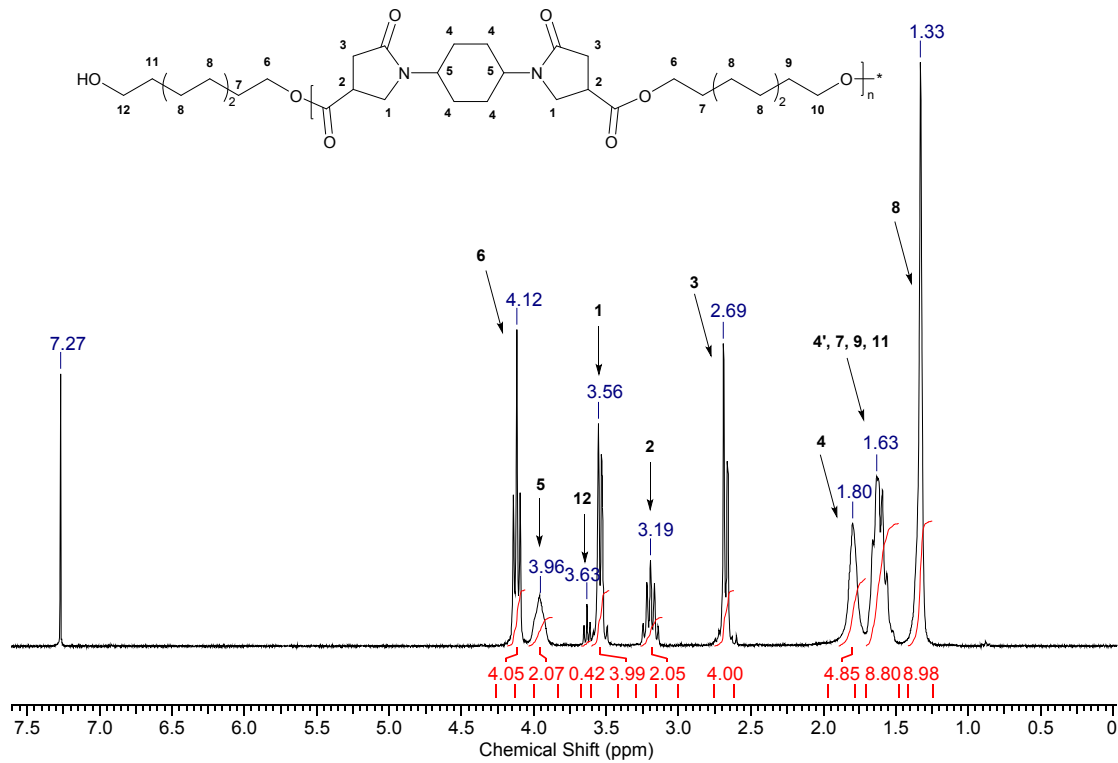


Figure 32. ¹H NMR analysis of poly([t-CH-BPDA]-C₈).

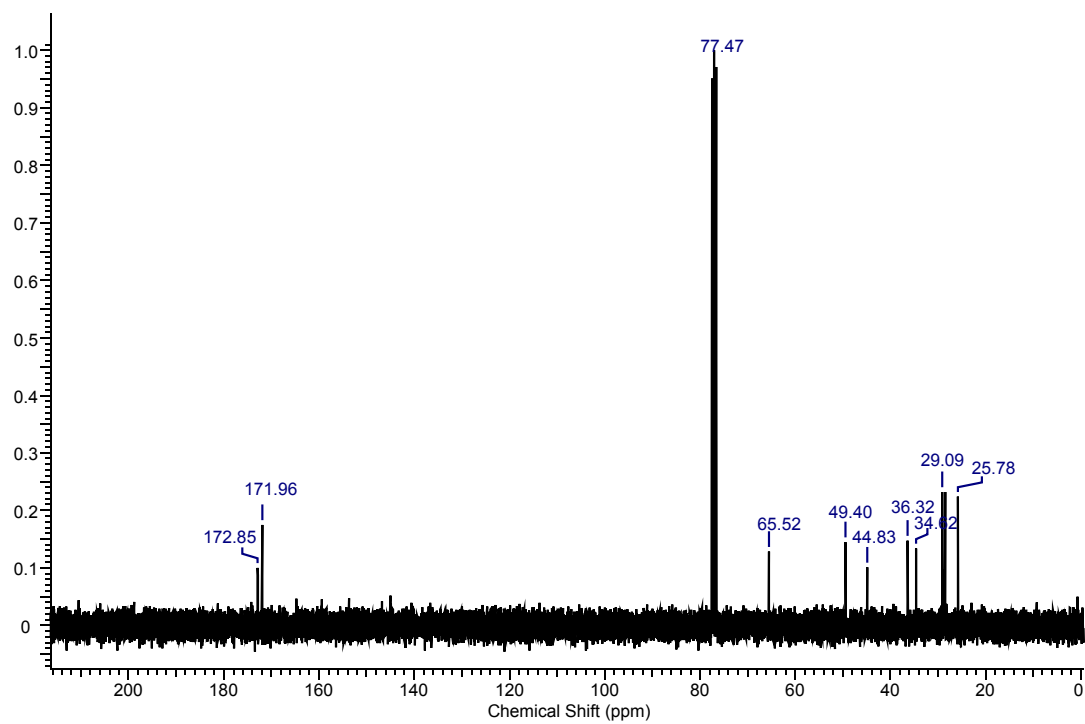


Figure 33. ¹³C NMR analysis of poly([t-CH-BPDA]-C₈).

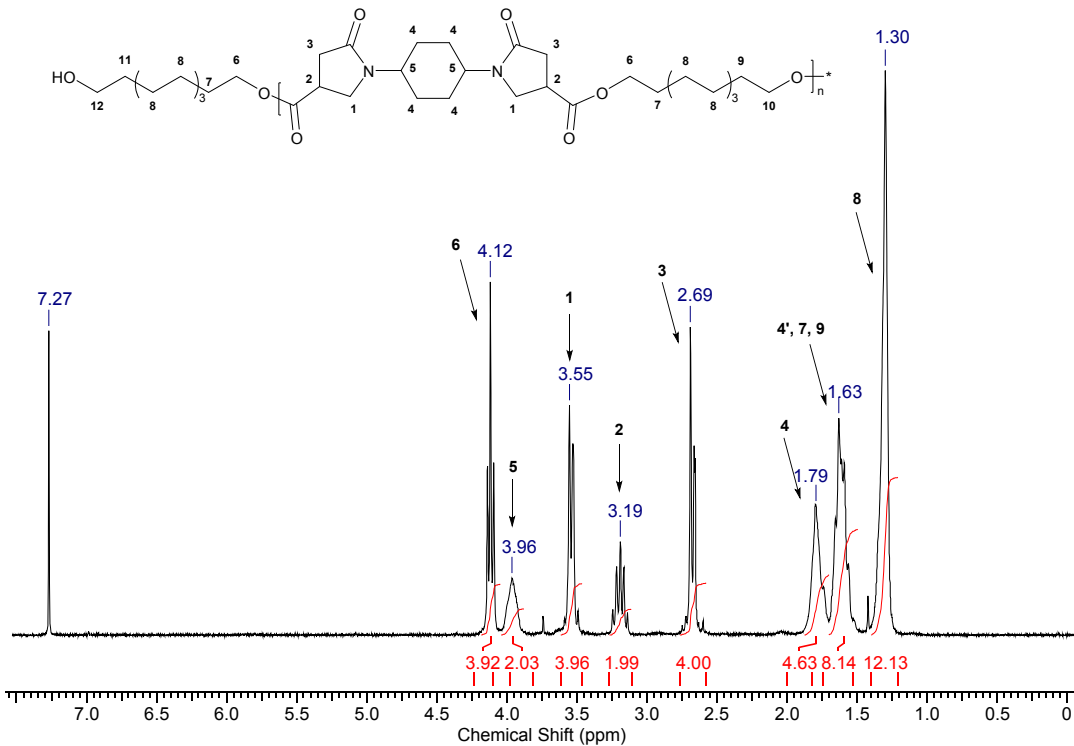


Figure 34. ¹H NMR analysis of poly([t-CH-BPDA]-C₁₀).

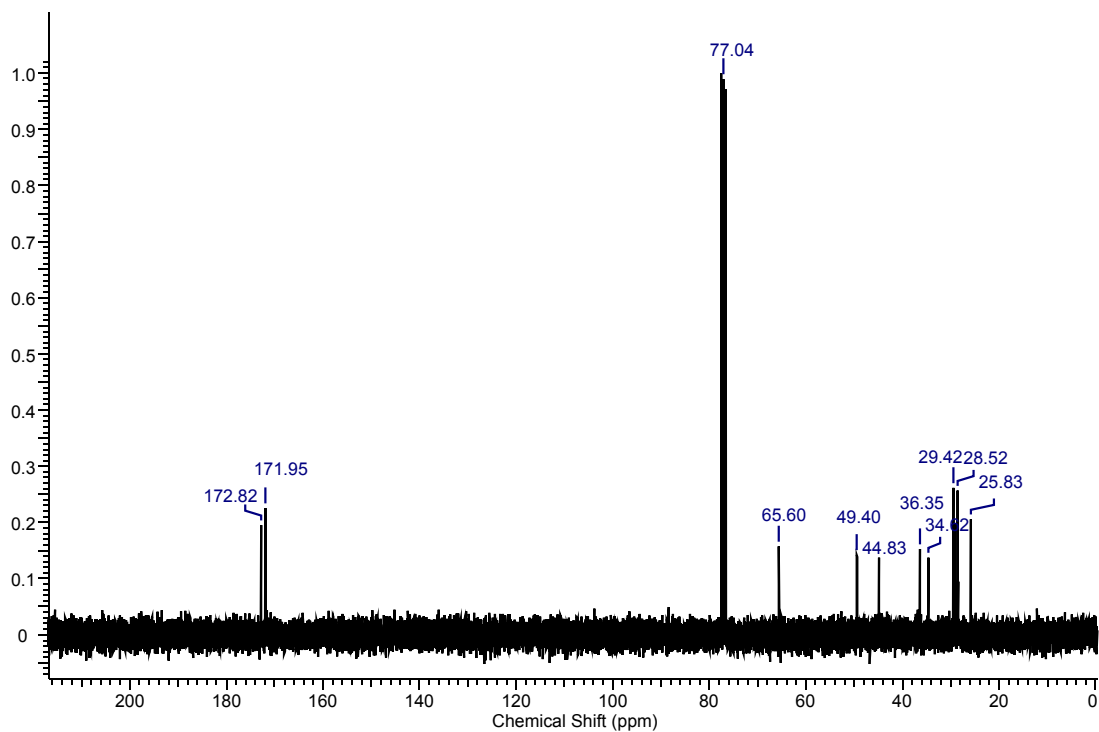


Figure 35. ¹³C NMR analysis of poly([t-CH-BPDA]-C₁₀).

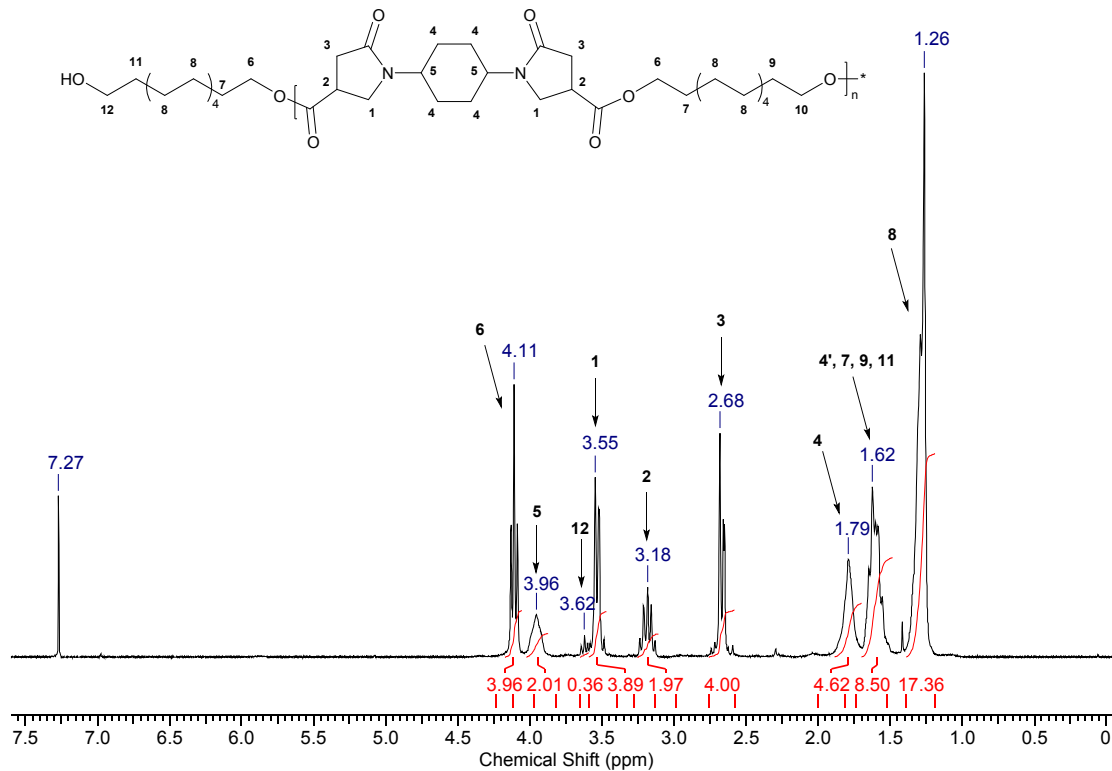


Figure 36. ¹H NMR analysis of poly([t-CH-BPDA]-C₁₂).

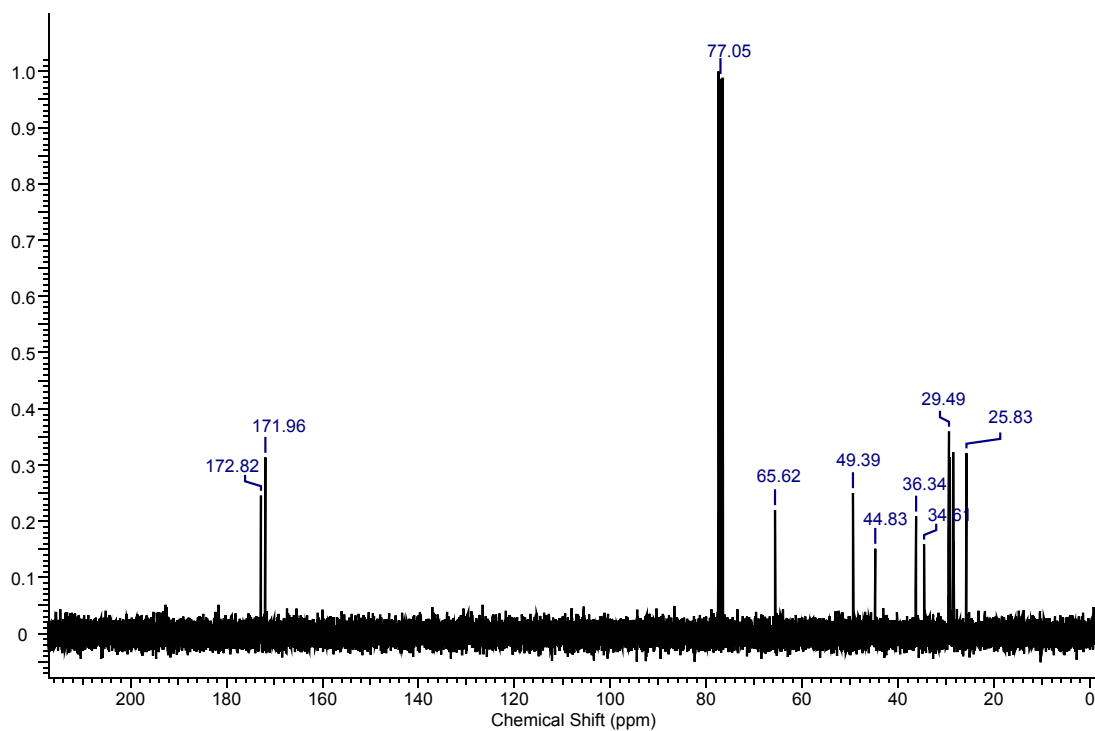


Figure 37. ¹³C NMR analysis of poly([t-CH-BPDA]-C₁₂).

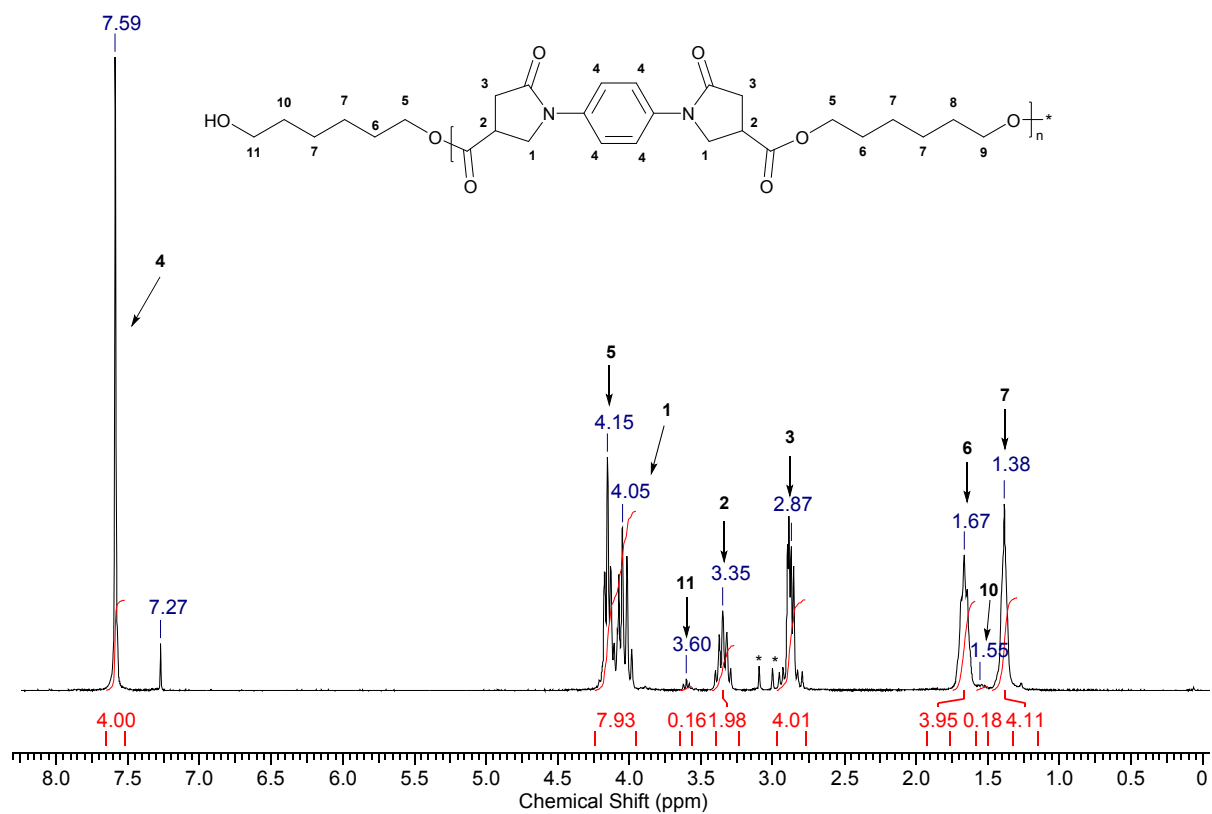


Figure 38. ¹H NMR analysis of poly([p-Ph-BPDA]-C₆), traces of DMF are denoted with an *.

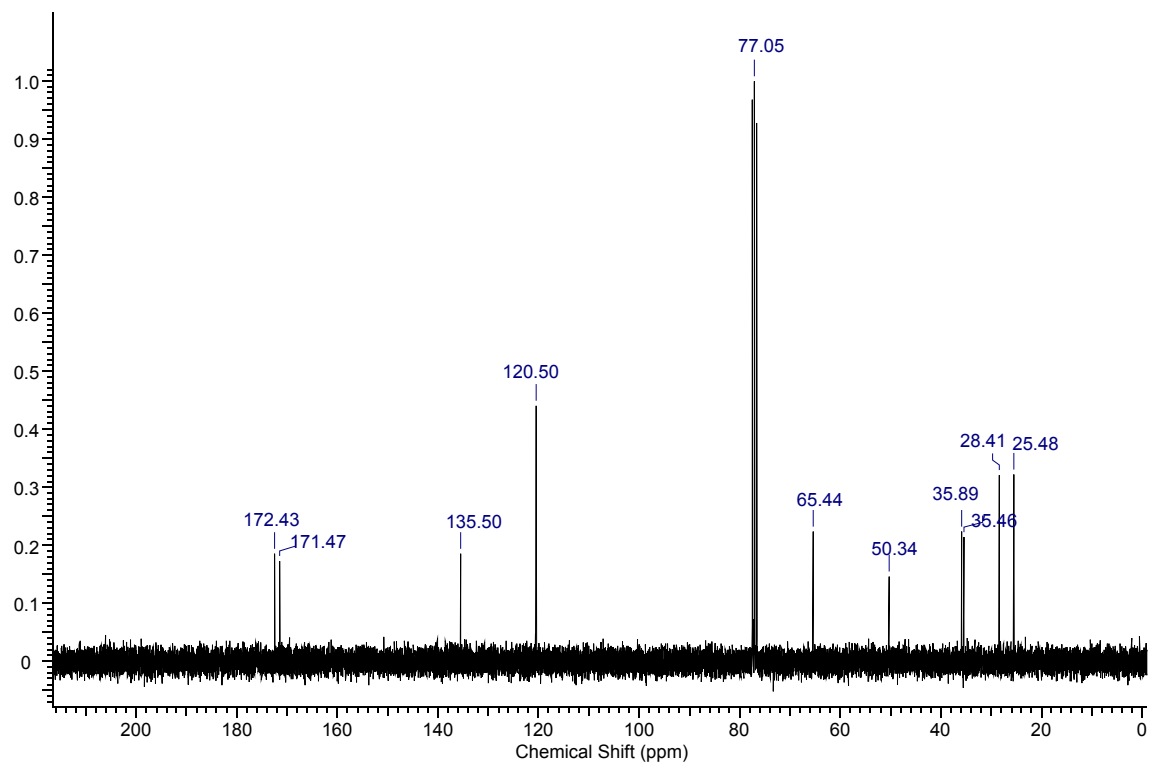


Figure 39. ¹³C NMR analysis of poly([p-Ph-BPDA]-C₆).

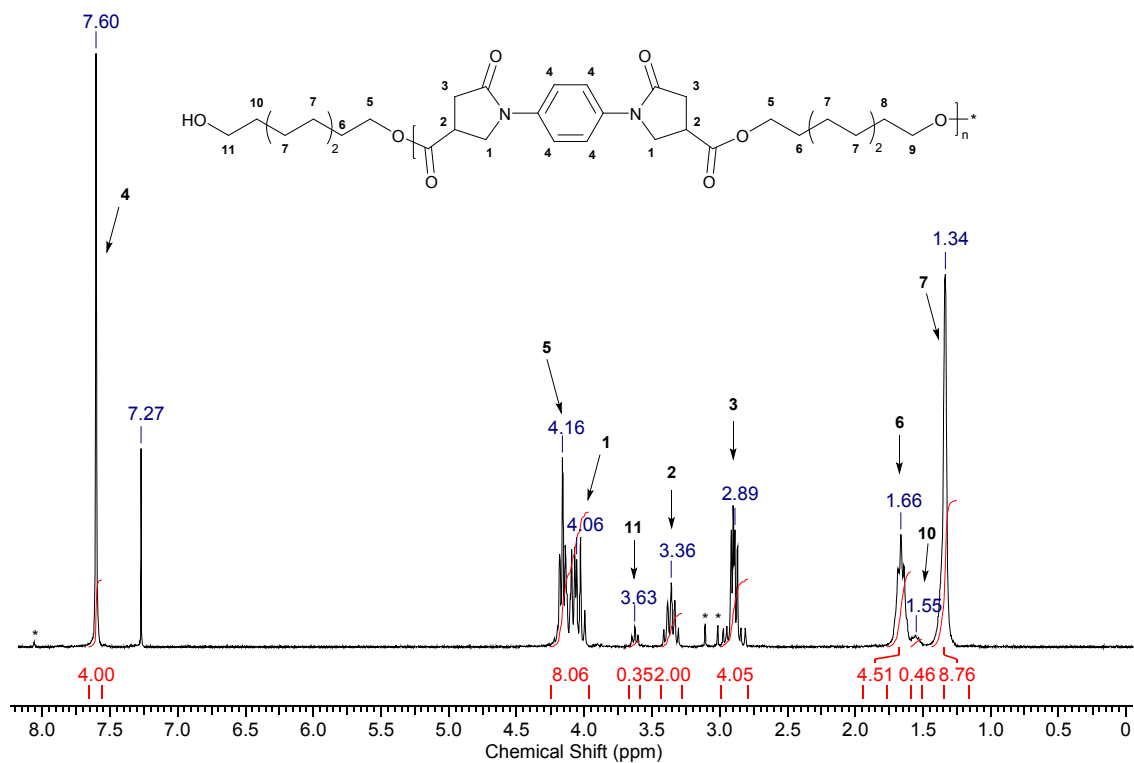


Figure 40. ¹H NMR analysis of poly([p-Ph-BPDA]-C₈), traces of DMF are denoted with an *.

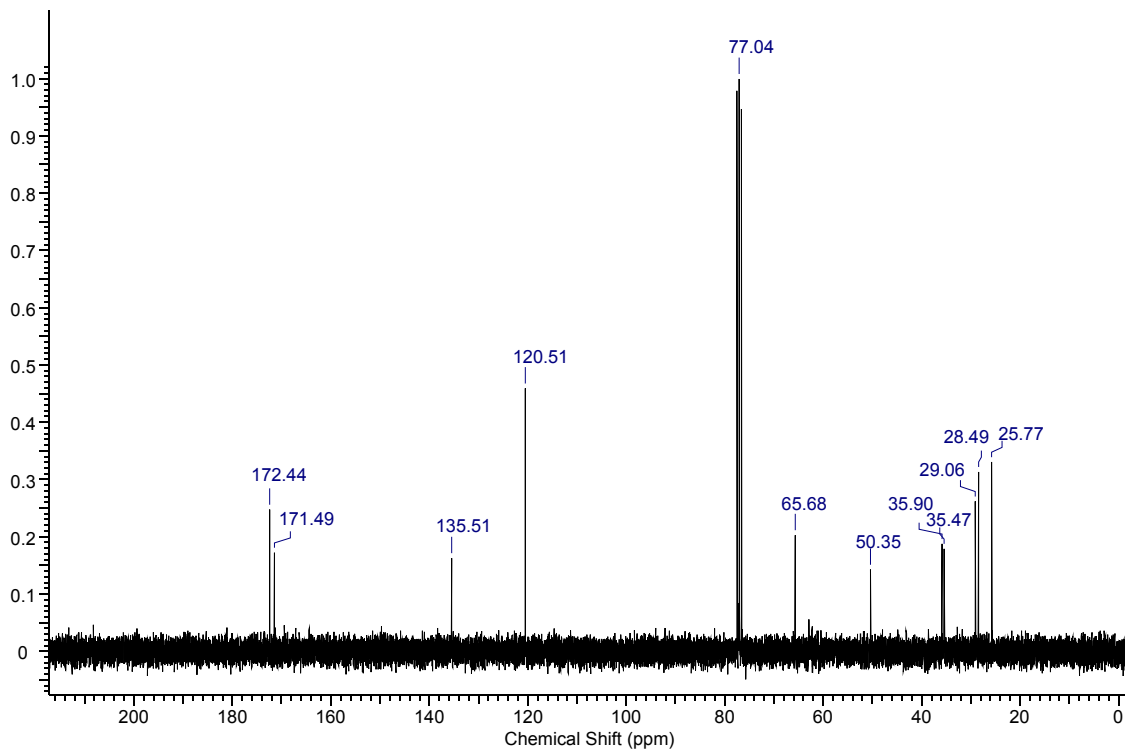


Figure 41. ¹³C NMR analysis of poly([p-Ph-BPDA]-C₈).

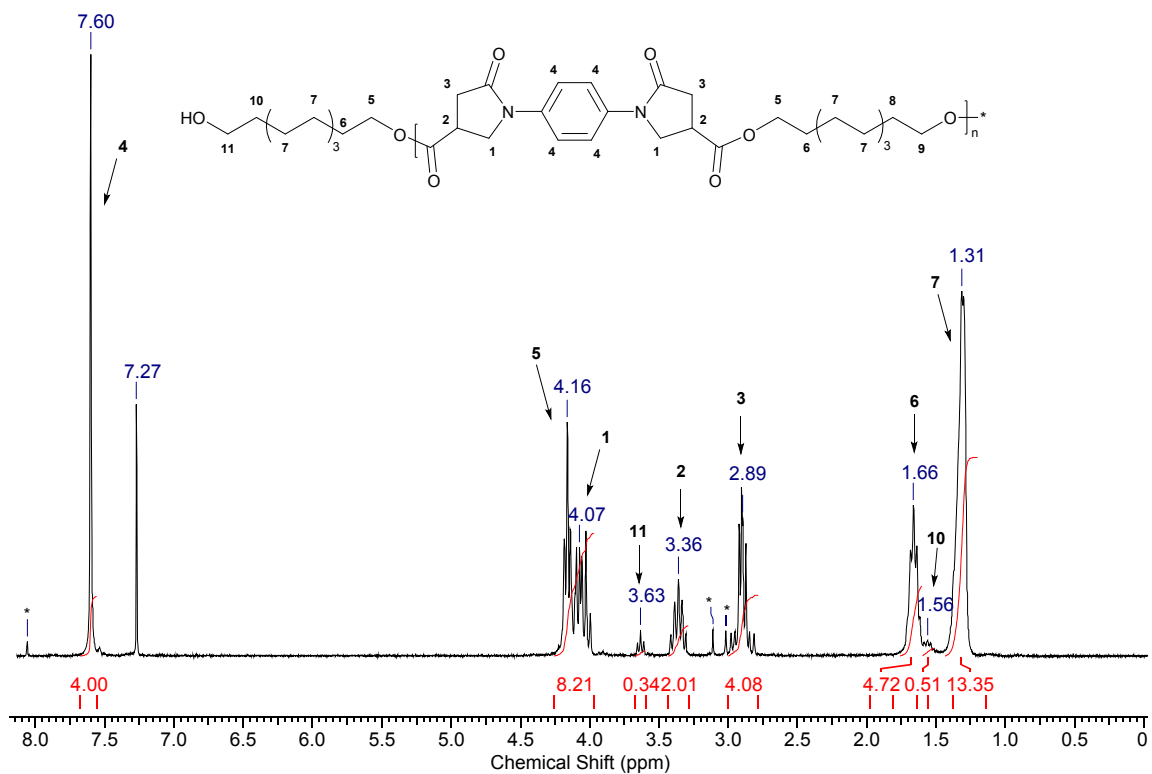


Figure 42. ¹H NMR analysis of poly([p-Ph-BPDA]-C₁₀), traces of DMF are denoted with *.

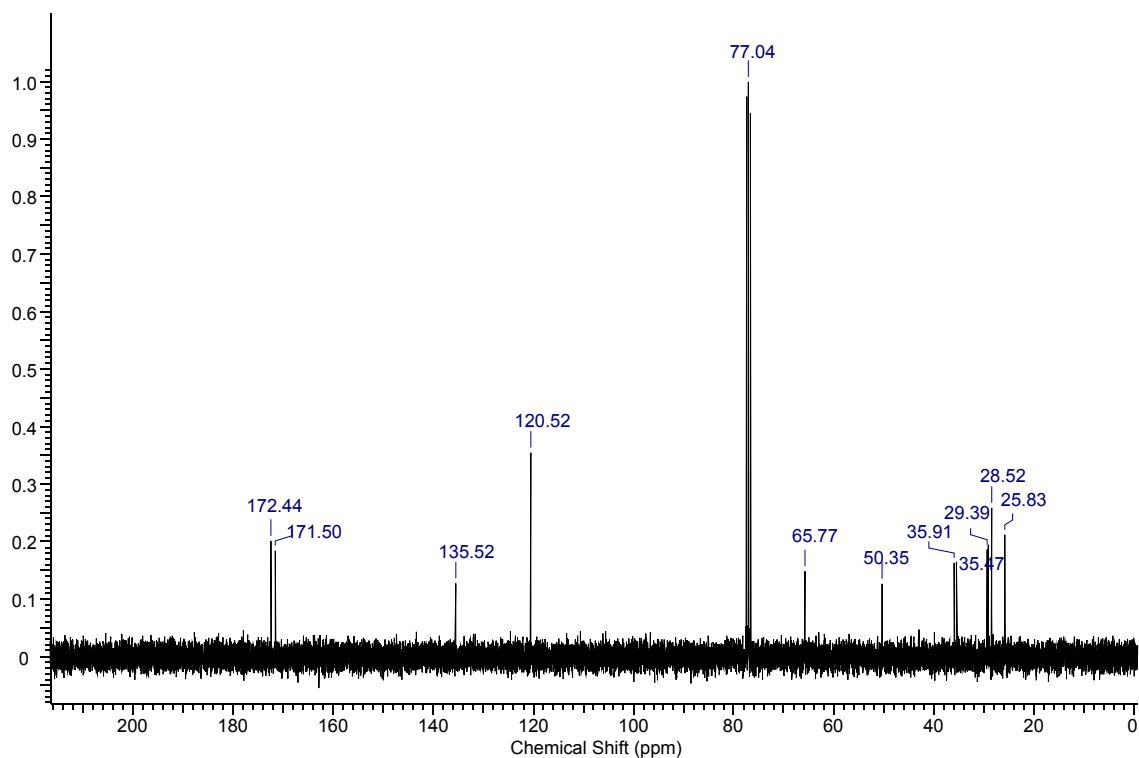


Figure 43. ¹³C NMR analysis of poly([p-Ph-BPDA]-C₁₀).

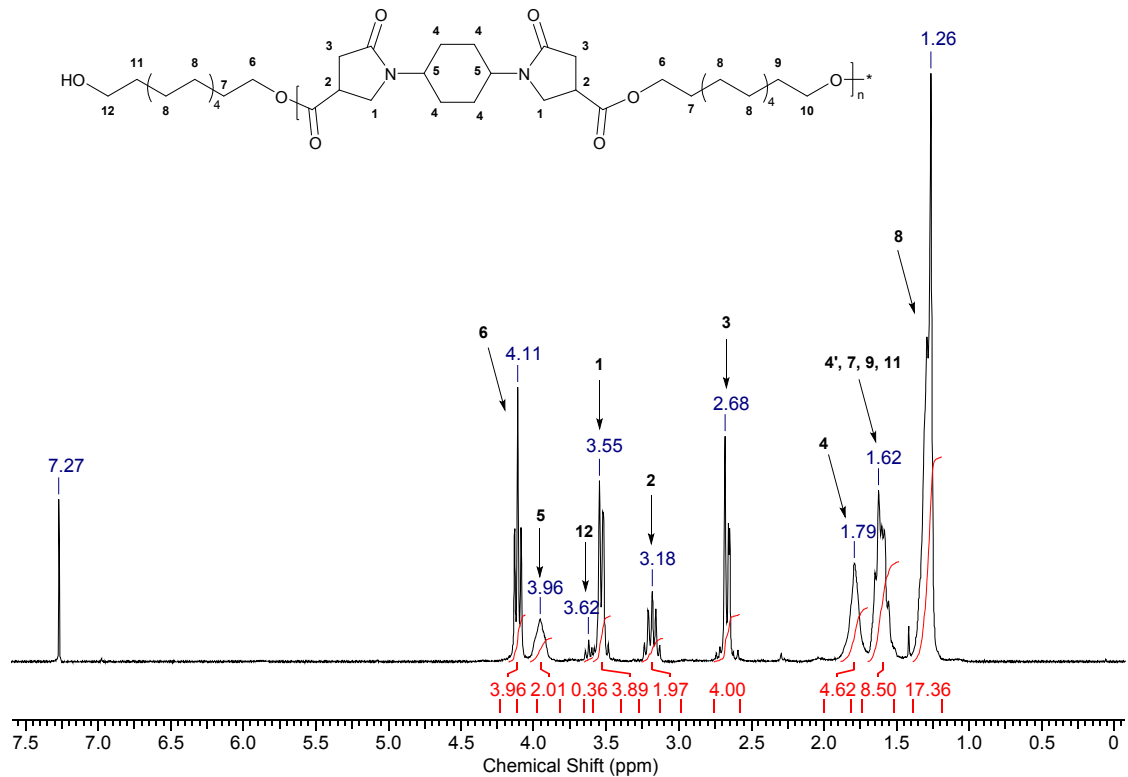


Figure 44. ¹H NMR analysis of poly([p-Ph-BPDA]-C₁₂).

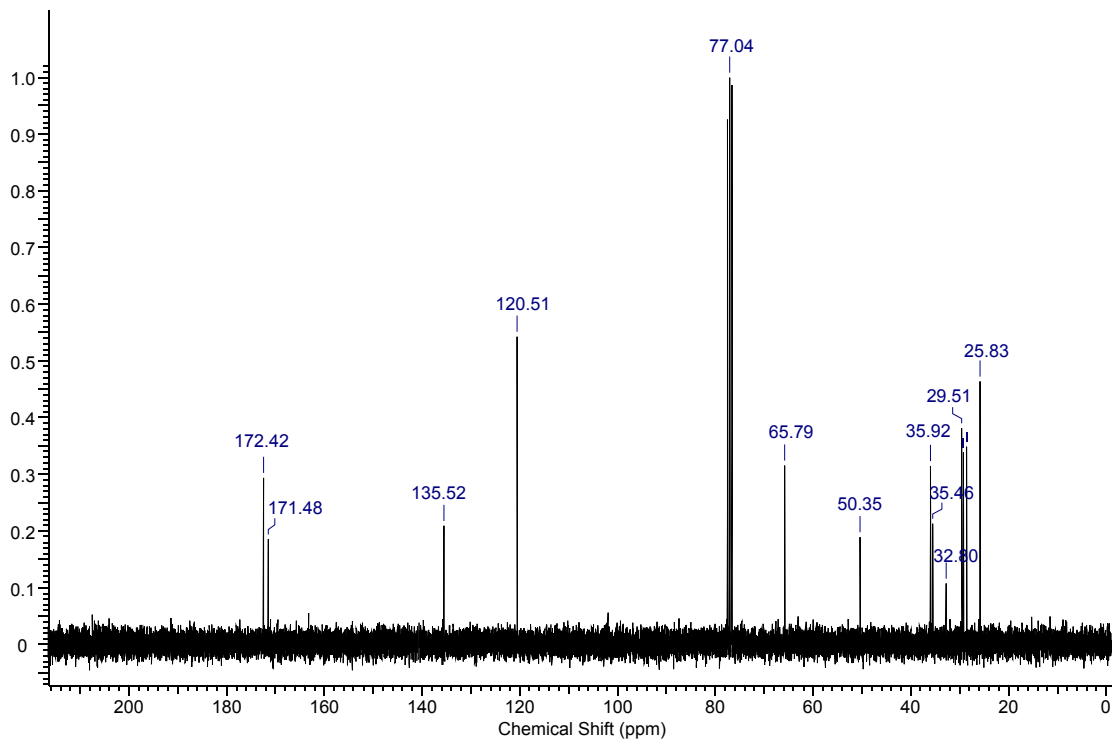


Figure 45. ¹³C NMR analysis of poly([p-Ph-BPDA]-C₁₂).

IR analysis of BPDA-based polyesters

Infra-red analysis was performed on the polymers based on *p*-Ph-BPDA(-dm) and *t*-CH-BPDA(-dm), reported in Table 3 and Table 4 of the manuscript, whereas the results are shown in Figures 46 and 47. In general we can detect the presence of the pyrrolidone ring by the resonances around 1420 cm^{-1} (*t*-CH-BPDA) or 1390 cm^{-1} (*p*-Ph-BPDA) and 1680 cm^{-1} , corresponding to the vibration of the tertiary amide group in the pyrrolidone ring and the carbonyl stretch of the pyrrolidone amide. Similarly, the carbonyl stretch of the carboxylic ester is observed at around 1750 cm^{-1} . Lastly, the presence of the phenyl ring in the *p*-Ph-BPDA(-dm) based polymers (Figure 47) is detected by the vibration of the aromatic ring around 820 and 1520 cm^{-1} .

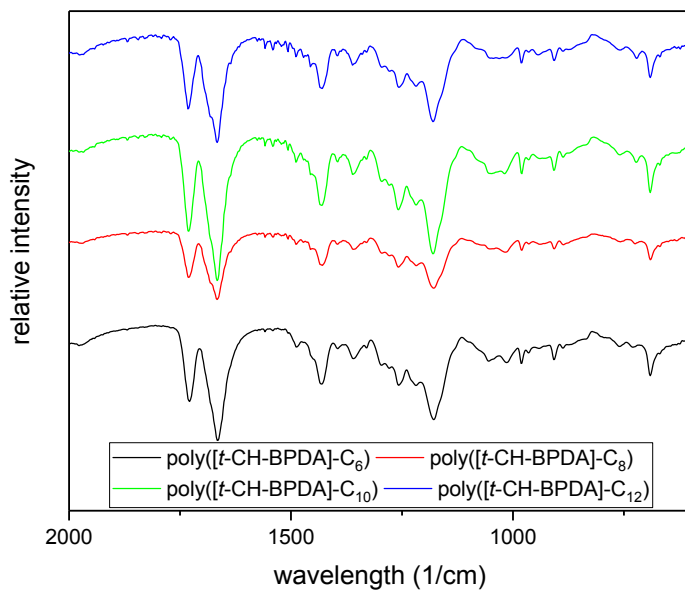


Figure 46. IR spectra for *t*-CH-BPDA-dm based polyesters, collected at room temperature. Poly([*t*-CH-BPDA]-C₆) (black), poly([*t*-CH-BPDA]-C₈) (red), Poly([*t*-CH-BPDA]-C₁₀) (green), and poly([*t*-CH-BPDA]-C₁₂) (blue).

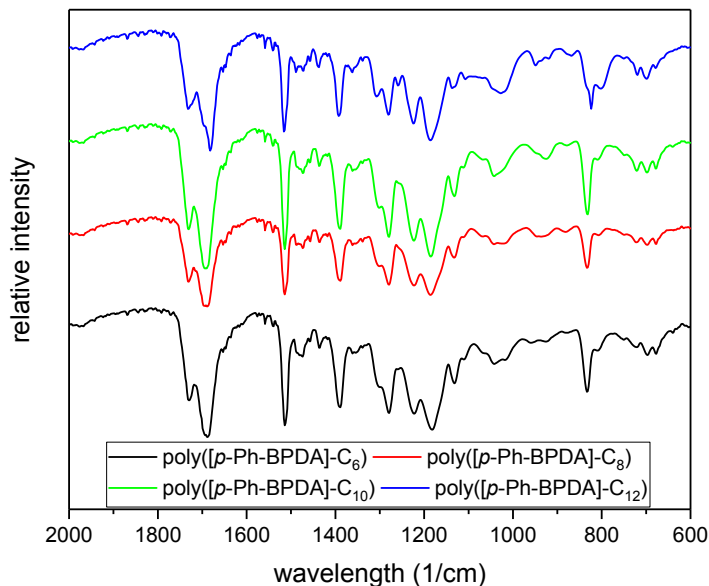


Figure 47. IR spectra for *p*-Ph-BPDA-dm based polyesters, collected at room temperature. Poly([*p*-Ph-BPDA]-C₆), poly([*p*-Ph-BPDA]-C₈), poly([*p*-Ph-BPDA]-C₁₀), and poly([*p*-Ph-BPDA]-C₁₂).

DSC analysis of BPDA-based polyesters

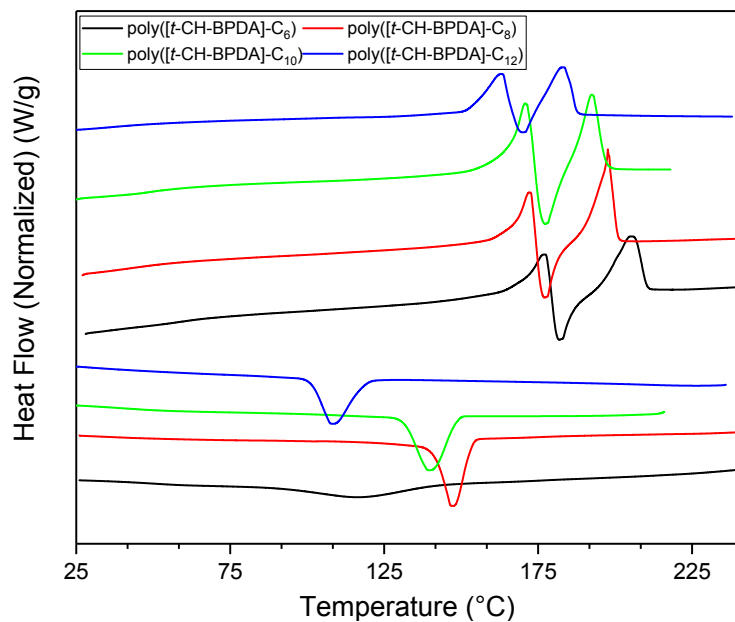


Figure 48. DSC thermograms of *t*-CH-BPDA-based polyesters. Bottom: first cooling of poly([*t*-CH-BPDA]-C₁₂) (blue, top), poly([*t*-CH-BPDA]-C₁₀) (green, 2nd), poly([*t*-CH-BPDA]-C₈) (red, 3rd), and poly([*t*-CH-BPDA]-C₆) (black, 4th). Top: second heating of poly([*t*-CH-BPDA]-C₁₂) (blue, top), poly([*t*-CH-BPDA]-C₁₀) (green, 2nd), poly([*t*-CH-BPDA]-C₈) (red, 3rd), and poly([*t*-CH-BPDA]-C₆) (black, 4th). Heating and cooling rate of 10 °C/min was used.

TGA water absorption test

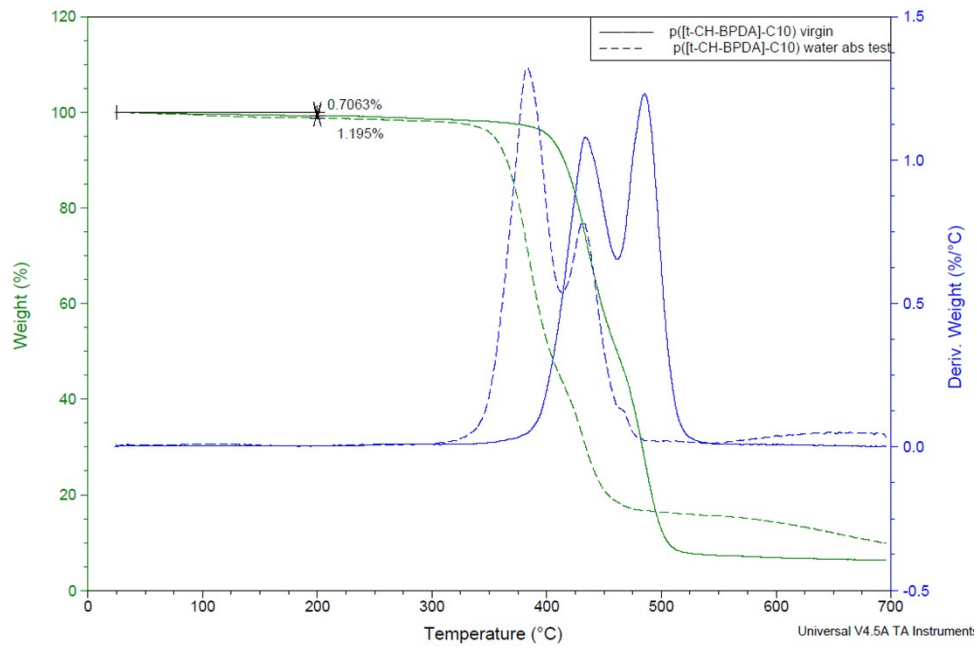


Figure 49. TGA analysis of water absorption of poly([t-CH-BPDA]-C₁₀). Solid line: virgin material (0.71 w% loss), dotted line: after 4 weeks in water (1.2 w% loss).