Electronic Supplementary Material (ESI) for Polymer Chemistry.

One-pot Cascade Polycondensation and Passerini Three-Component Reactions for the Synthesis of Functional Polyesters

Burcu Alkan[1,2], Ozgun Daglar[1], Serter Luleburgaz[1], Begum Gungor[1], Ufuk Saim Gunay[1], Gurkan Hizal[1], Umit Tunca[1], Hakan Durmaz[1*]

[1]*Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey*

[2]*Yalova Vocational School, University of Yalova, 77200 Yalova, Turkey*

E-mail: durmazh@itu.edu.tr

Synthetic Procedures

Synthesis of P1

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), BD (82.6 mg, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.75 mmol, 3 equiv) and CHI (342 µL, 2.75 mmol, 3 equiv) were used. The resulting white sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 681 mg, 90%). ^{1}H NMR ($CDCl_3$, δ) 8.27-7.27 (m, 10H, Ar*H*), 7.20-7.07 (br, 2H, N*H*), 6.33 (br, 2H, OC*H*C=O), 4.36 (br, 4H, OCH_2), 3.76 (br, 2H, NHC*H*), 1.86-1.09 (m, 24H, cyclohexyl and main chain CH_2); ^{13}C NMR ($CDCl_3$, δ) 165.89, 165.68, 164.43, 148.14, 137.03, 133.94, 130.79, 129.80, 123.87, 122.03, 76.19, 66.25, 48.88, 32.56, 25.38, 24.82.

Synthesis of P2

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), 1,4-cyclohexanedimethanol (132 mg, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.75 mmol, 3 equiv) and CHI (342 µL, 2.75 mmol, 3 equiv) were used. The resulting white sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 799 mg, 99%). ^{1}H NMR ($CDCl_3$, δ) 8.27-7.56 (m, 10H, Ar*H*), 7.16-7.06 (br, 2H, N*H*), 6.34 (d, 2H, OC*H*C=O), 4.35-4.15 (m, 4H, C=OOCH_2), 3.78 (br, 2H, NHC*H*), 1.91-1.05 (m, 28H, aliphatic protons of cyclohexane); ^{13}C NMR ($CDCl_3$, δ) 165.81, 164.52, 148.23, 137.10, 134.02, 129.82, 123.93, 121.90, 76.25, 71.75, 48.88, 36.71, 32.61, 28.60, 25.46, 24.86.

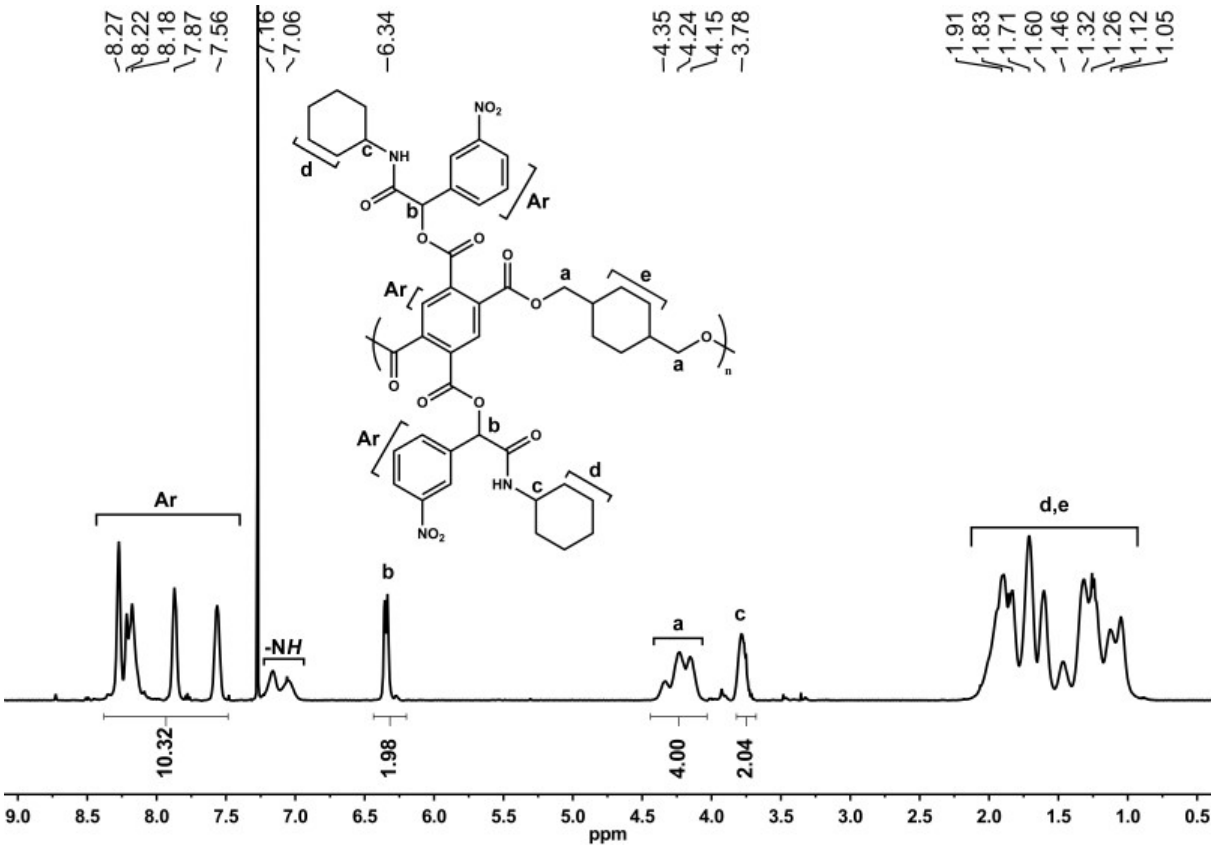

Fig. S1. ^{1}H NMR spectrum of **P2** in $CDCl_3$ (500 MHz).

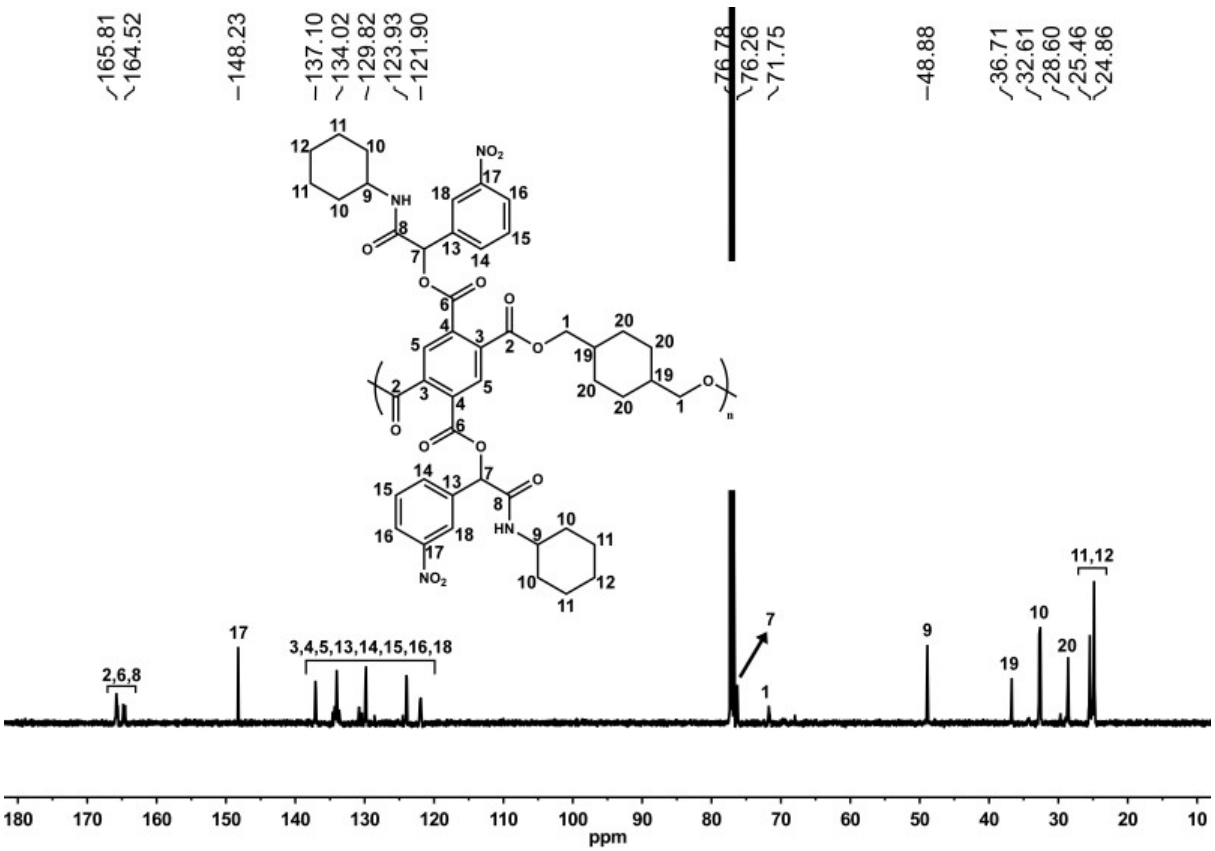

Fig. S2. ^{13}C NMR spectrum of **P2** in $CDCl_3$ (125 MHz).

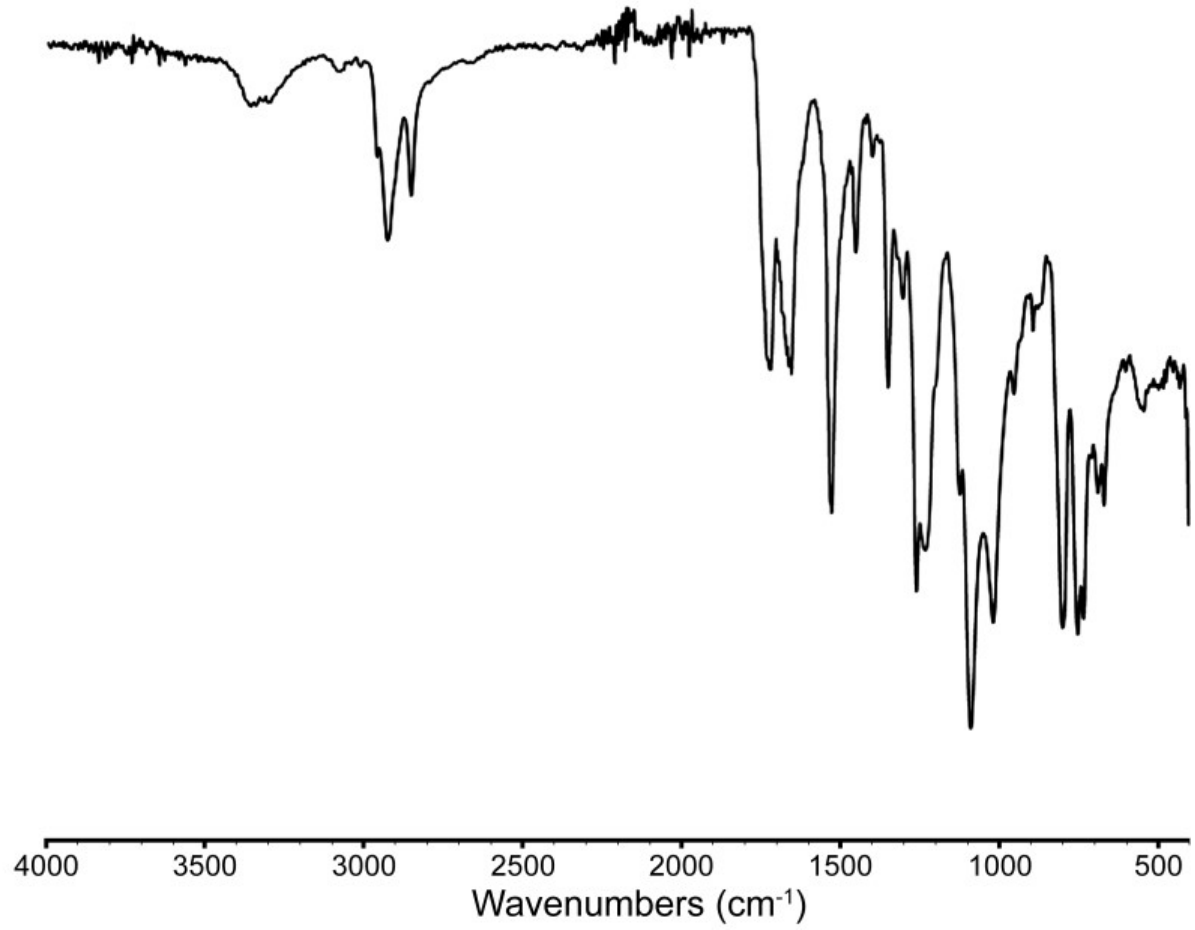

Fig. S3. FT-IR spectrum of **P2**.

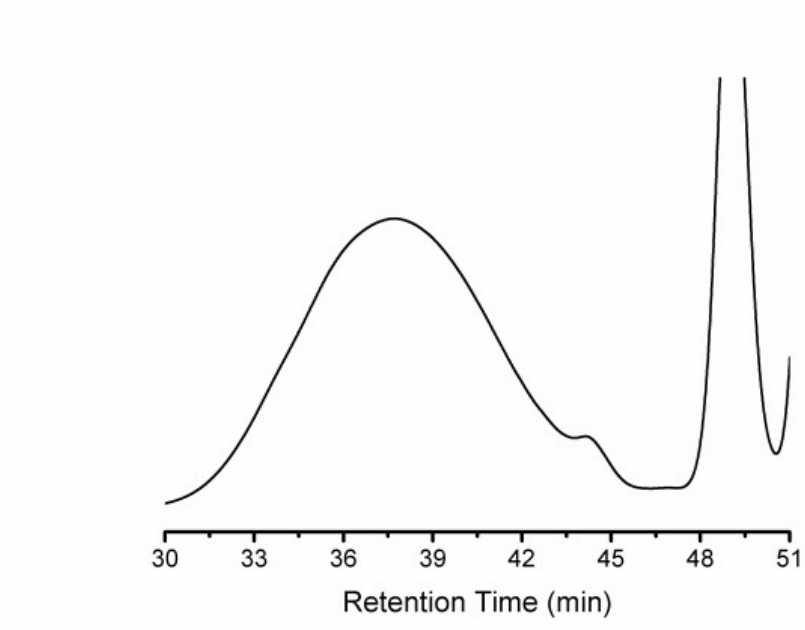

Fig. S4. GPC trace of **P2.**

Synthesis of P3

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), tetraethylene glycol (178 mg, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.75 mmol, 3 equiv) and CHI (342 µL, 2.75 mmol, 3 equiv) were used. The resulting white sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 491 mg, 57%). ^{1}H NMR ($CDCl_3$, δ) 8.30-7.56 (m, 10H, Ar*H*), 7.15-7.03 (br, 2H, N*H*), 6.34 (s, 2H, OC*H*C=O), 4.51-4.39 (m, 4H, C=OOCH_2), 3.77-3.65 (m, 14H, OCH_2 of tetraethylene glycol and NHC*H*), 2.06-1.12 (m, 20H, CH_2 of cyclohexane); ^{13}C NMR ($CDCl_3$, δ) 165.91, 165.54, 164.73, 148.20, 137.12, 134.32, 133.91, 133.20, 130.87, 129.84, 123.92, 122.09, 77.04, 70.36, 68.48, 65.93, 48.84, 32.73, 25.43, 24.88.

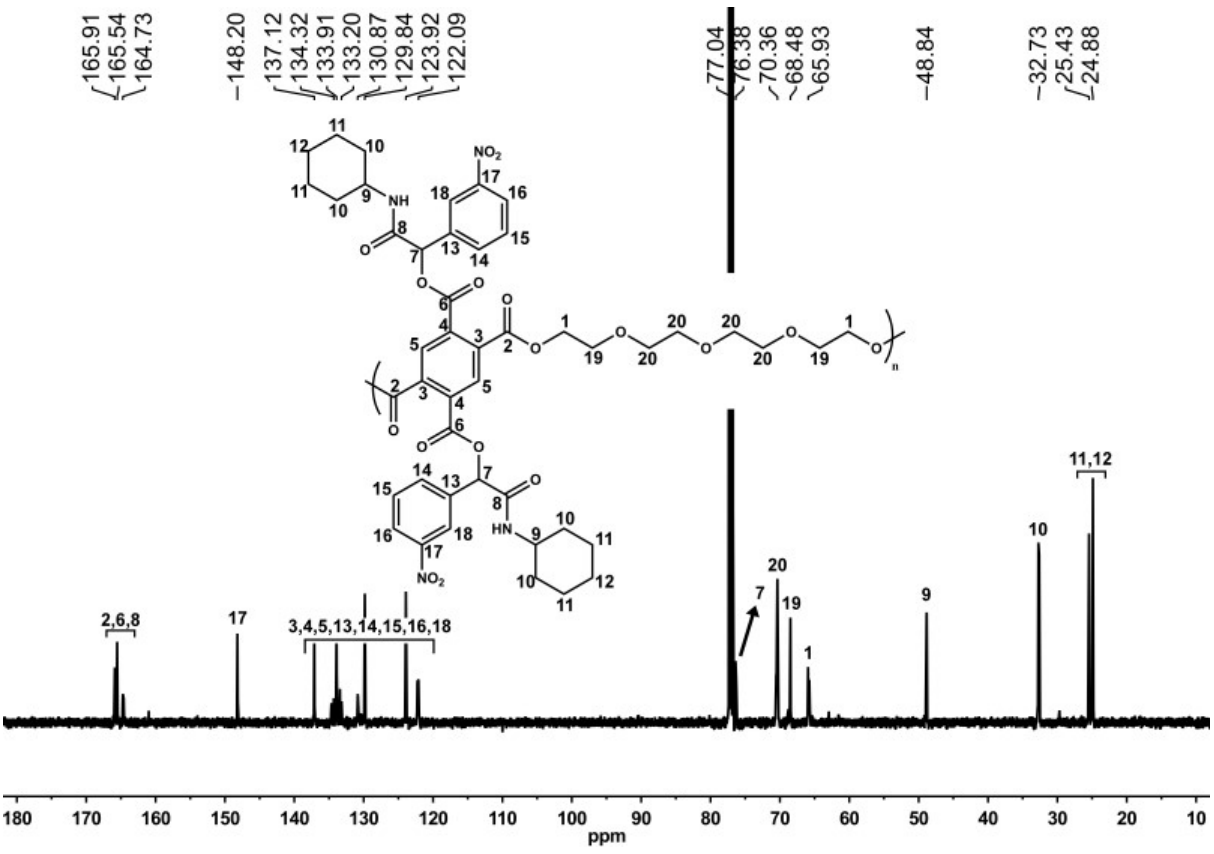

Fig. S5. ^{13}C NMR spectrum of **P3** in $CDCl_3$ (125 MHz).

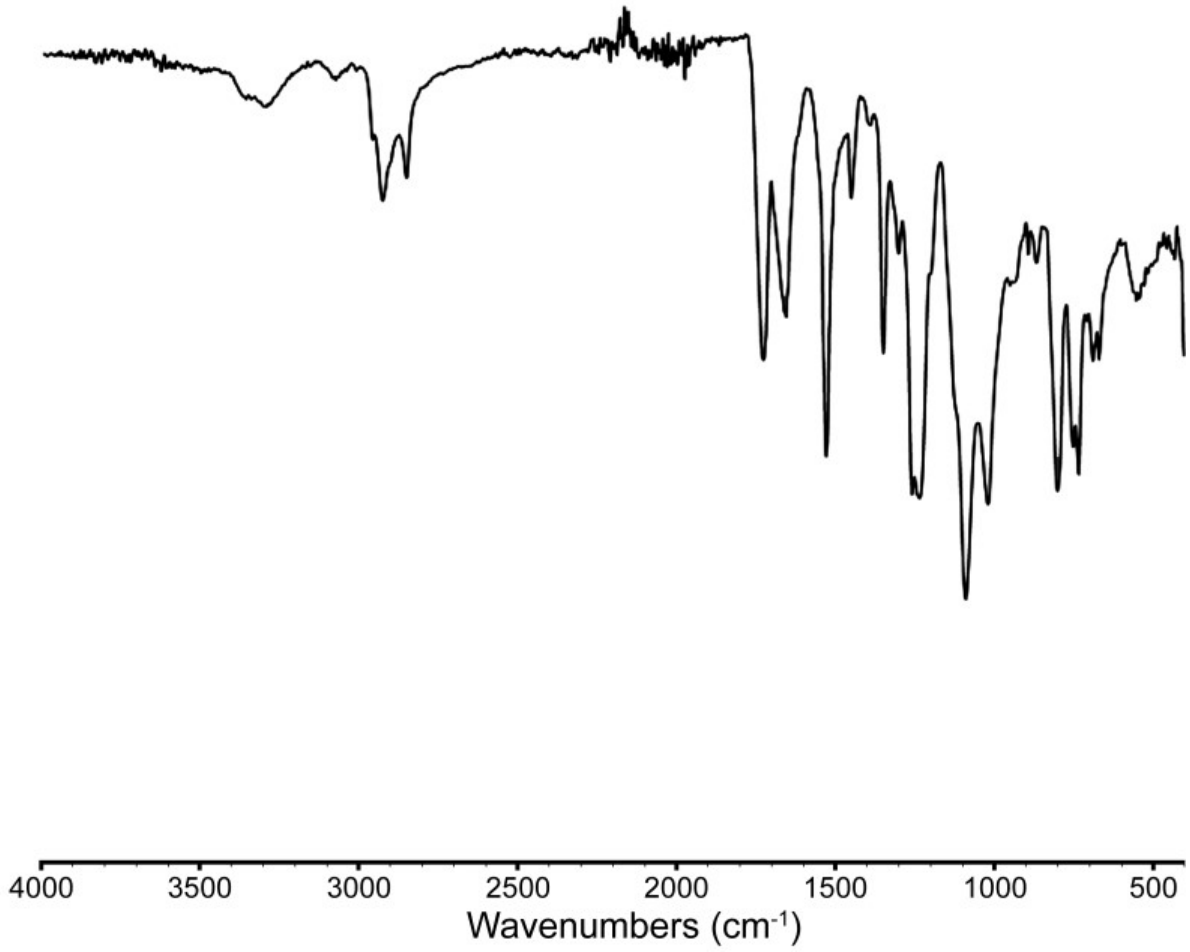

Fig. S6. FT-IR spectrum of **P3**.

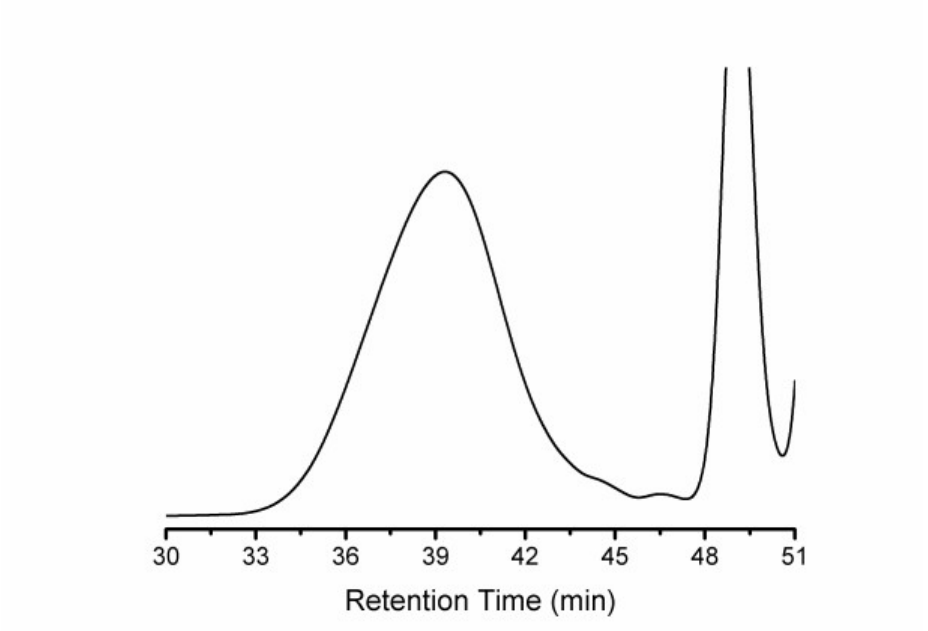

Fig. S7. GPC trace of **P3**.

Synthesis of P4

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), 2,2,3,3-tetrafluoro-1,4-butanediol (149 mg, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.75 mmol, 3 equiv) and CHI (342 µL, 2.75 mmol, 3 equiv) were used. The resulting white sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 629 mg, 76%). ^{1}H NMR ($CDCl_3$, δ) 8.20-7.51 (m, 10H, Ar*H*), 6.99 (br, 2H, N*H*), 6.32 (br, 2H, OC*H*C=O), 4.76 (br, 4H, C=OOCH_2CF$_2$), 3.75 (br, 2H, NHC*H*), 1.86-1.08 (m, 20H, CH_2 of cyclohexane); ^{13}C NMR ($CDCl_3$, δ) 165.76, 163.95, 148.11, 136.78, 133.78, 130.90, 129.86, 123.97, 122.17, 114.62, 76.40, 67.98, 48.92, 32.59, 25.61, 25.33, 24.75.

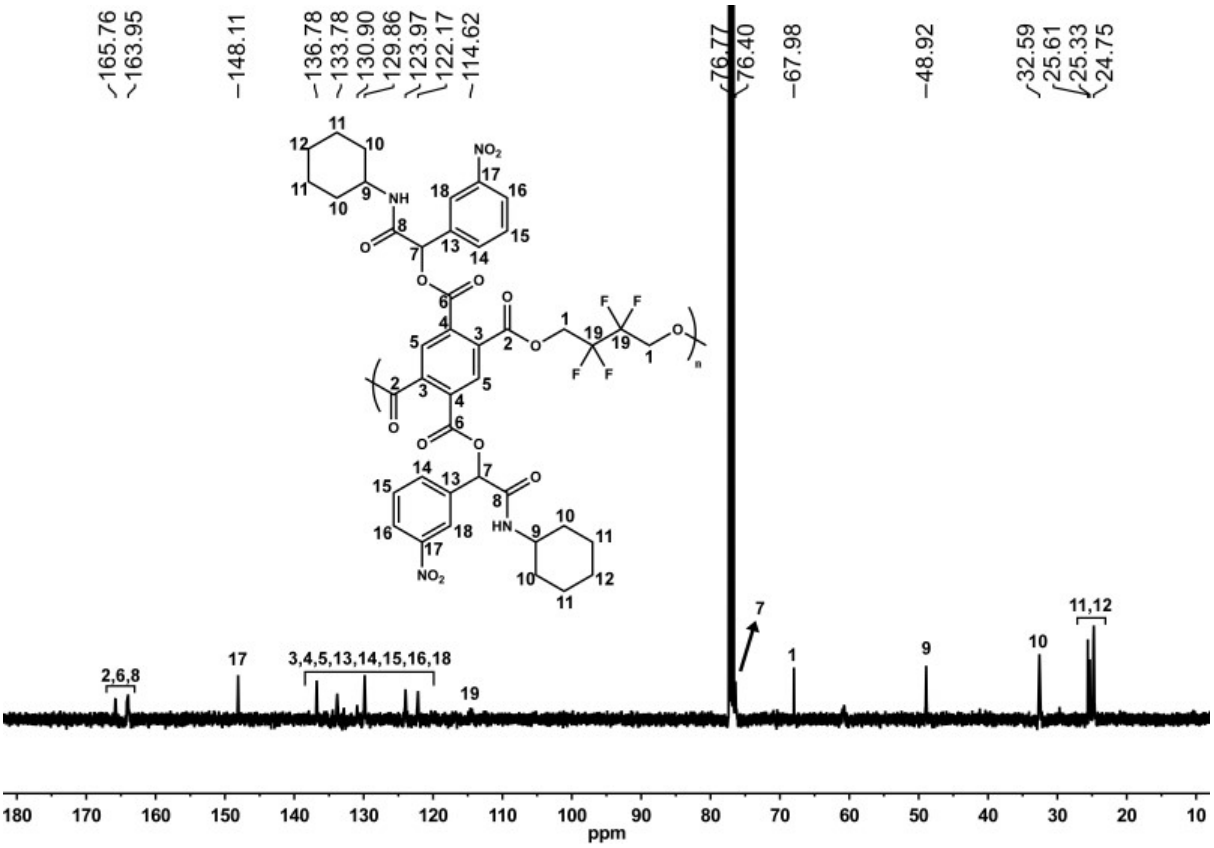

Fig. S8. ^{13}C NMR spectrum of **P4** in $CDCl_3$ (125 MHz).

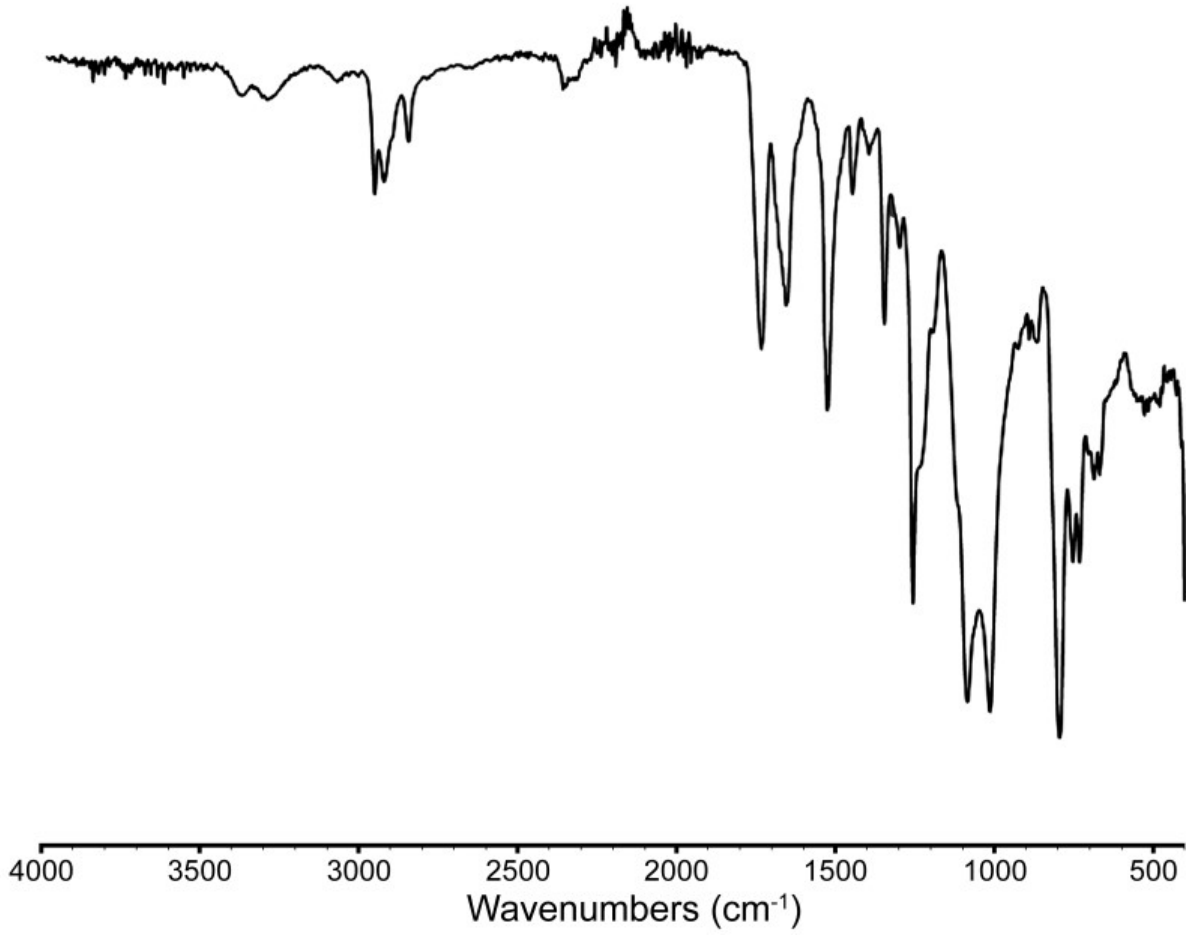

Fig. S9. FT-IR spectrum of **P4**.

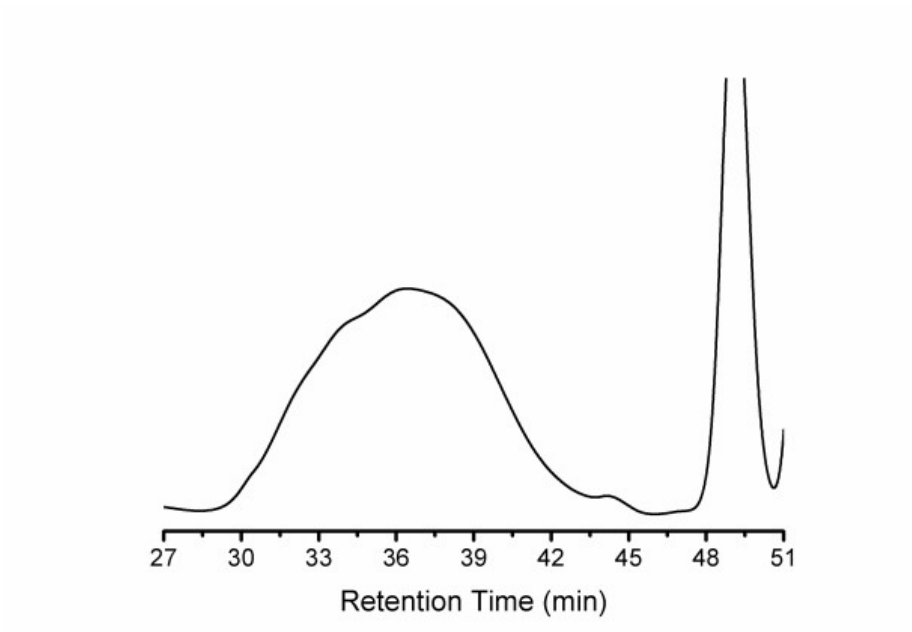

Fig. S10. GPC trace of **P4**.

Synthesis of P5

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), *cis*-2-butene-1,4-diol (75.4 µL, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.75 mmol, 3 equiv) and CHI (342 µL, 2.75 mmol, 3 equiv) were used. The resulting white sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 733 mg, 97%). ^{1}H NMR ($CDCl_3$, δ) 8.29-7.54 (m, 10H, Ar*H*), 7.10 (br, 2H, N*H*), 6.31 (br, 2H, OC*H*C=O), 5.84 (br, 2H, C=OOCH$_2$C*H*=), 4.95 (br, 4H, C=OOC*H*$_2$CH=), 3.75 (br, 2H, NHC*H*), 1.87-1.10 (m, 20H, C*H*$_2$ of cyclohexane); ^{13}C NMR ($CDCl_3$, δ) 165.94, 165.10, 164.58, 148.14, 136.97, 134.63, 133.86, 133.39, 130.68, 128.60, 127.85, 124.50, 123.91, 122.00, 77.29, 61.96, 48.88, 32.67, 25.37, 24.79.

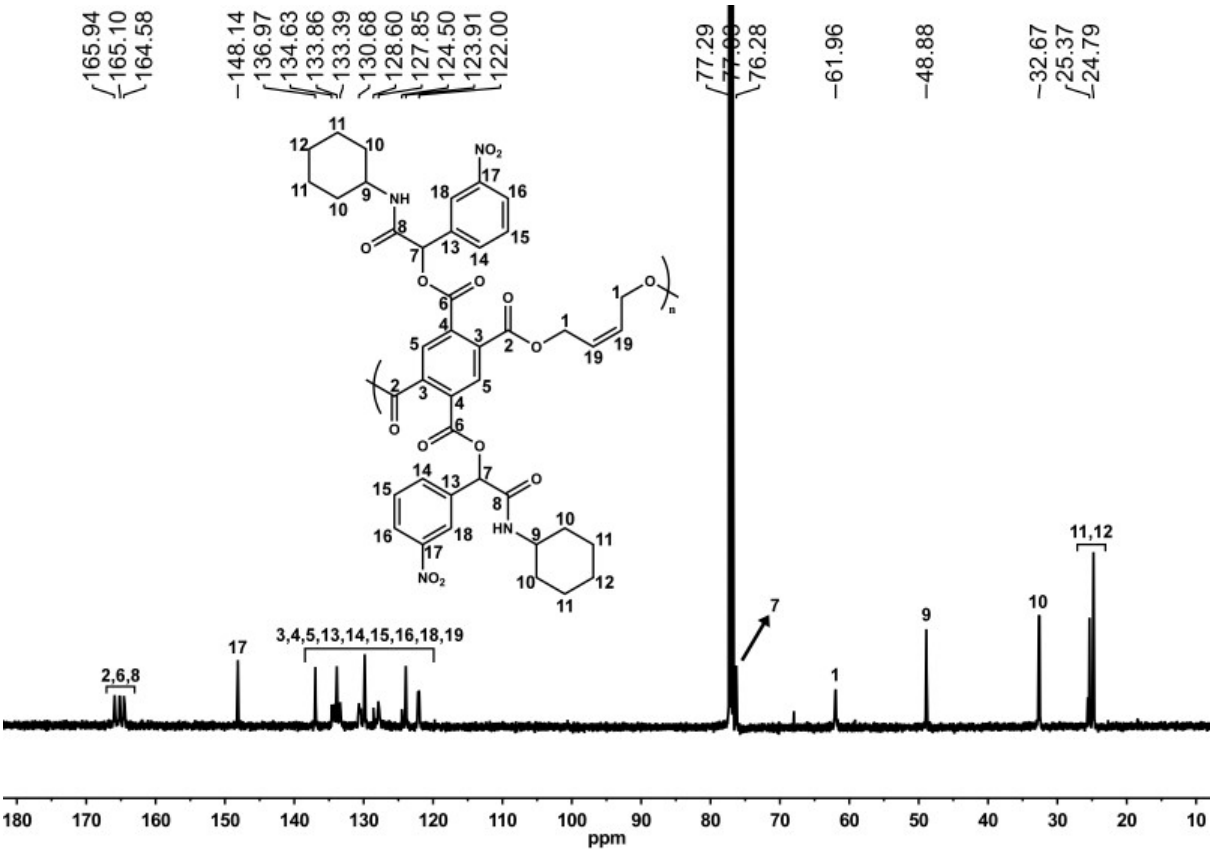

Fig. S11. ^{13}C NMR spectrum of **P5** in $CDCl_3$ (125 MHz).

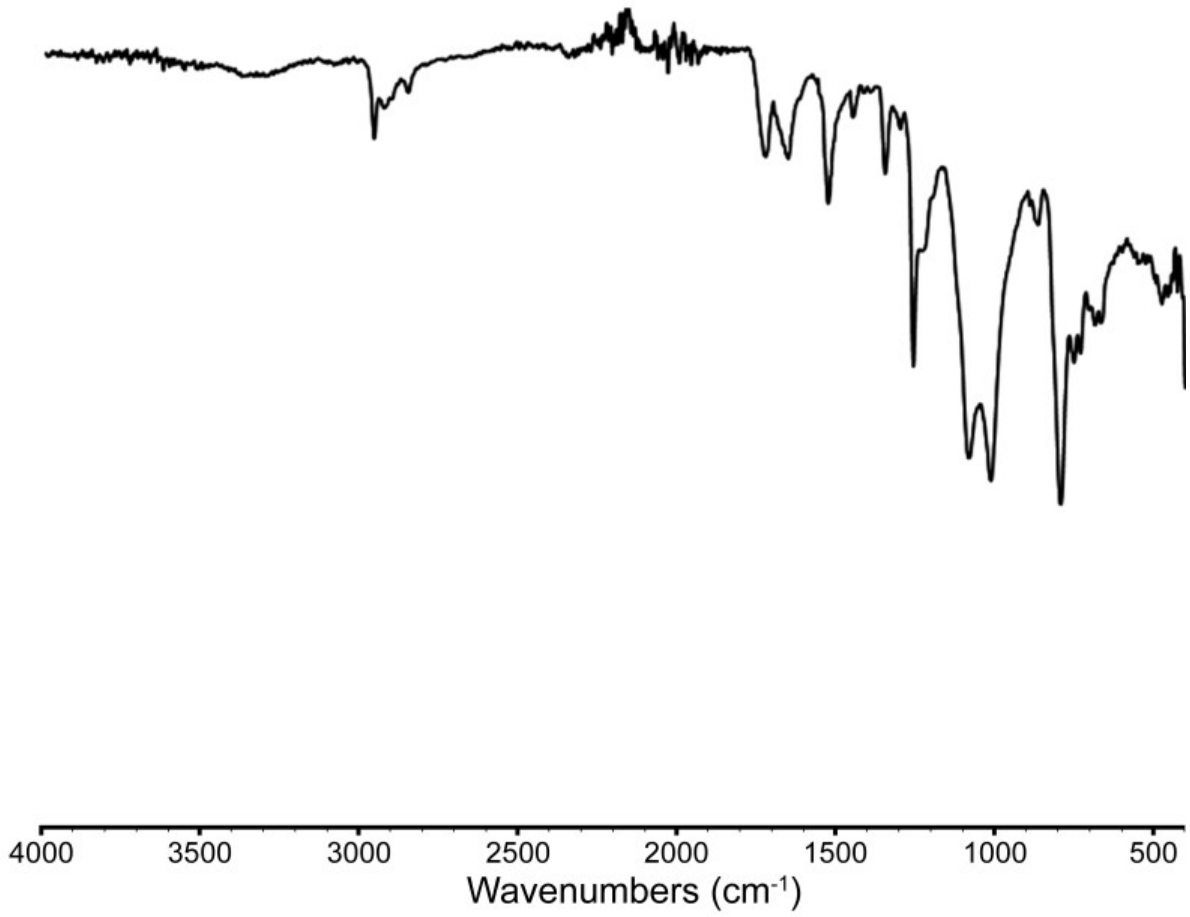

Fig. S12. FT-IR spectrum of **P5**.

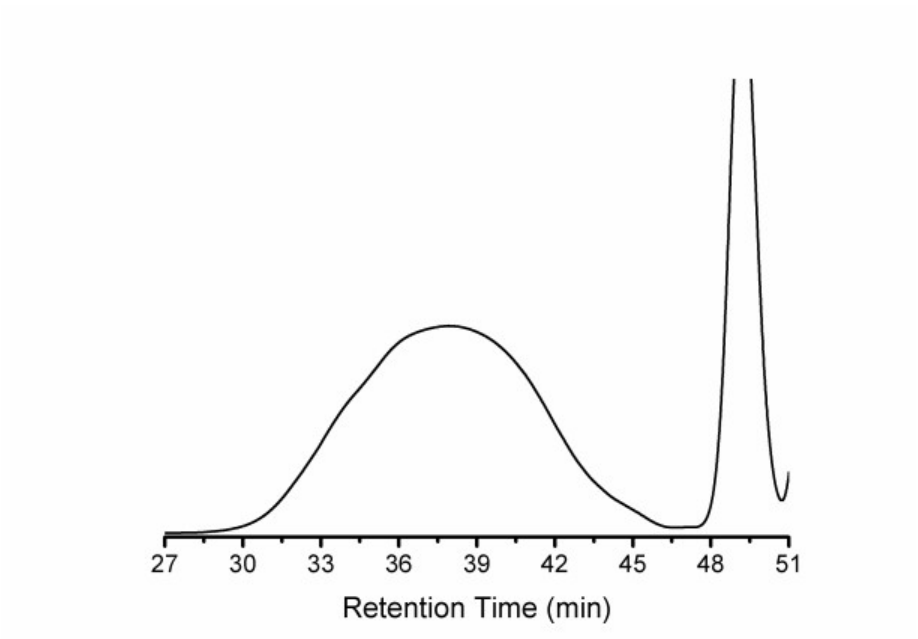

Fig. S13. GPC trace of **P5**.

Synthesis of P6

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), 2-butyne-1,4-diol (78.9 mg, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.75 mmol, 3 equiv) and CHI (342 μL, 2.75 mmol, 3 equiv) were used. The resulting white sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 742 mg, 98%). ^{1}H NMR ($CDCl_3$, δ) 8.28-7.54 (m, 10H, Ar*H*), 7.04 (br, 2H, N*H*), 6.32 (br, 2H, OC*H*C=O), 4.93 (br, 4H, C=OOCH_2C≡), 3.75 (br, 2H, NHC*H*), 1.87-1.09 (m, 20H, CH_2 of cyclohexane); ^{13}C NMR ($CDCl_3$, δ) 165.90, 165.20, 164.58, 148.14, 136.96, 134.63, 133.87, 133.39, 130.66, 129.86, 128.60, 127.89, 124.50, 123.91, 121.98, 77.24, 62.00, 48.88, 32.58, 25.37, 24.79.

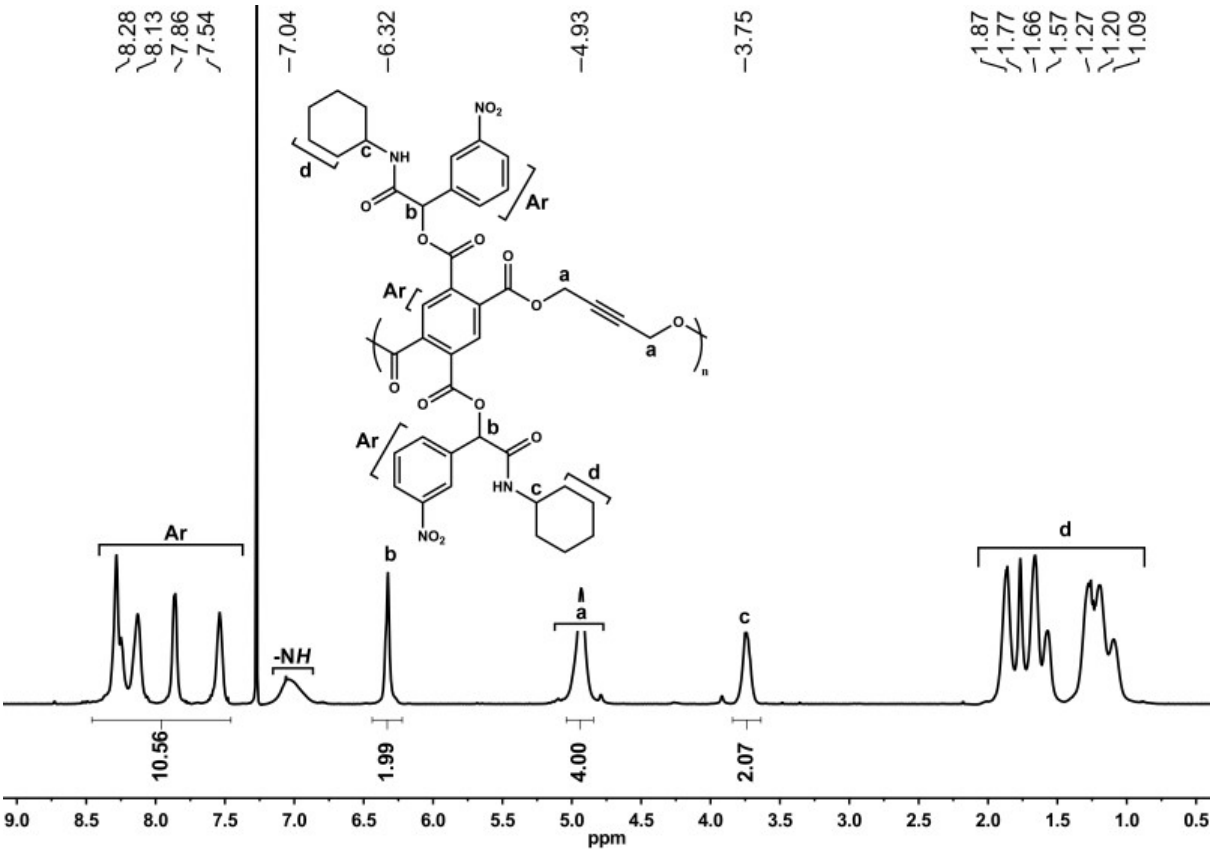

Fig. S14. ^{1}H NMR spectrum of **P6** in $CDCl_3$ (500 MHz).

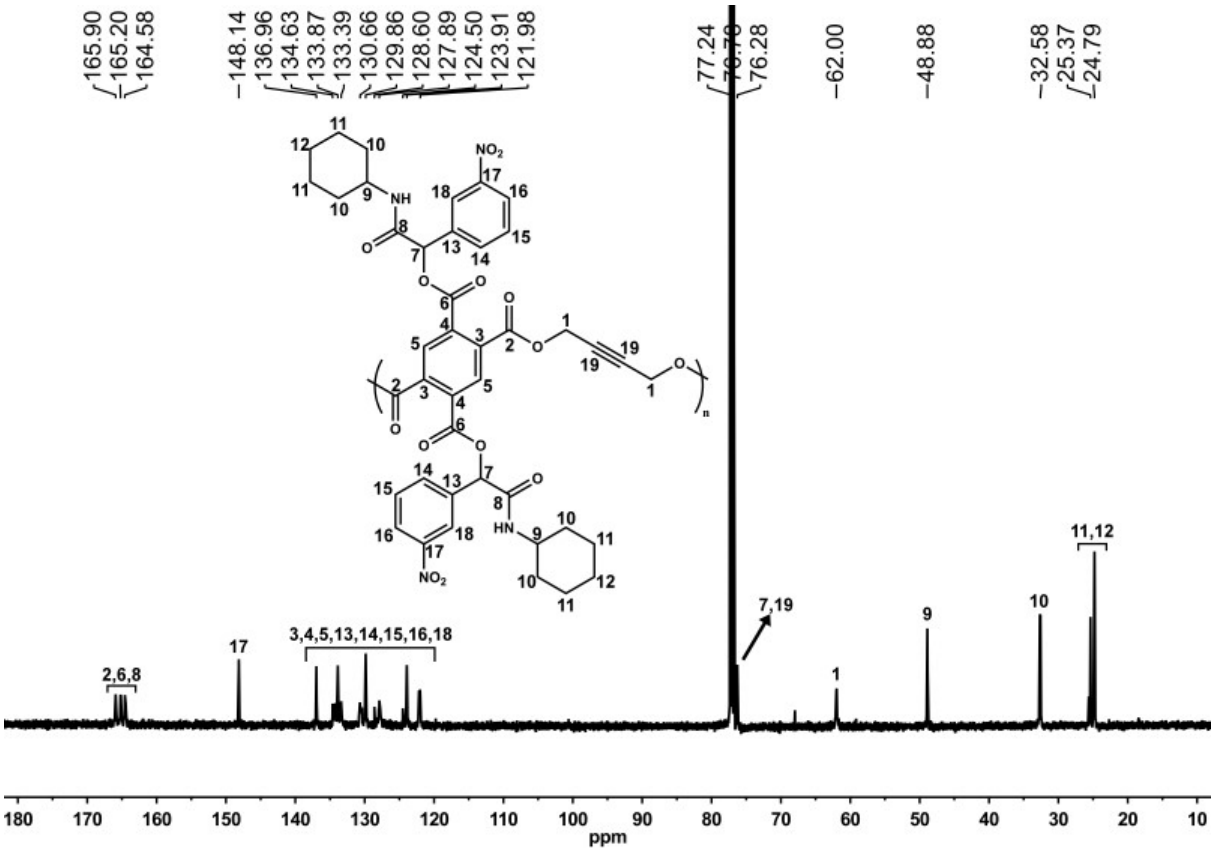

Fig. S15. ^{13}C NMR spectrum of **P6** in $CDCl_3$ (125 MHz).

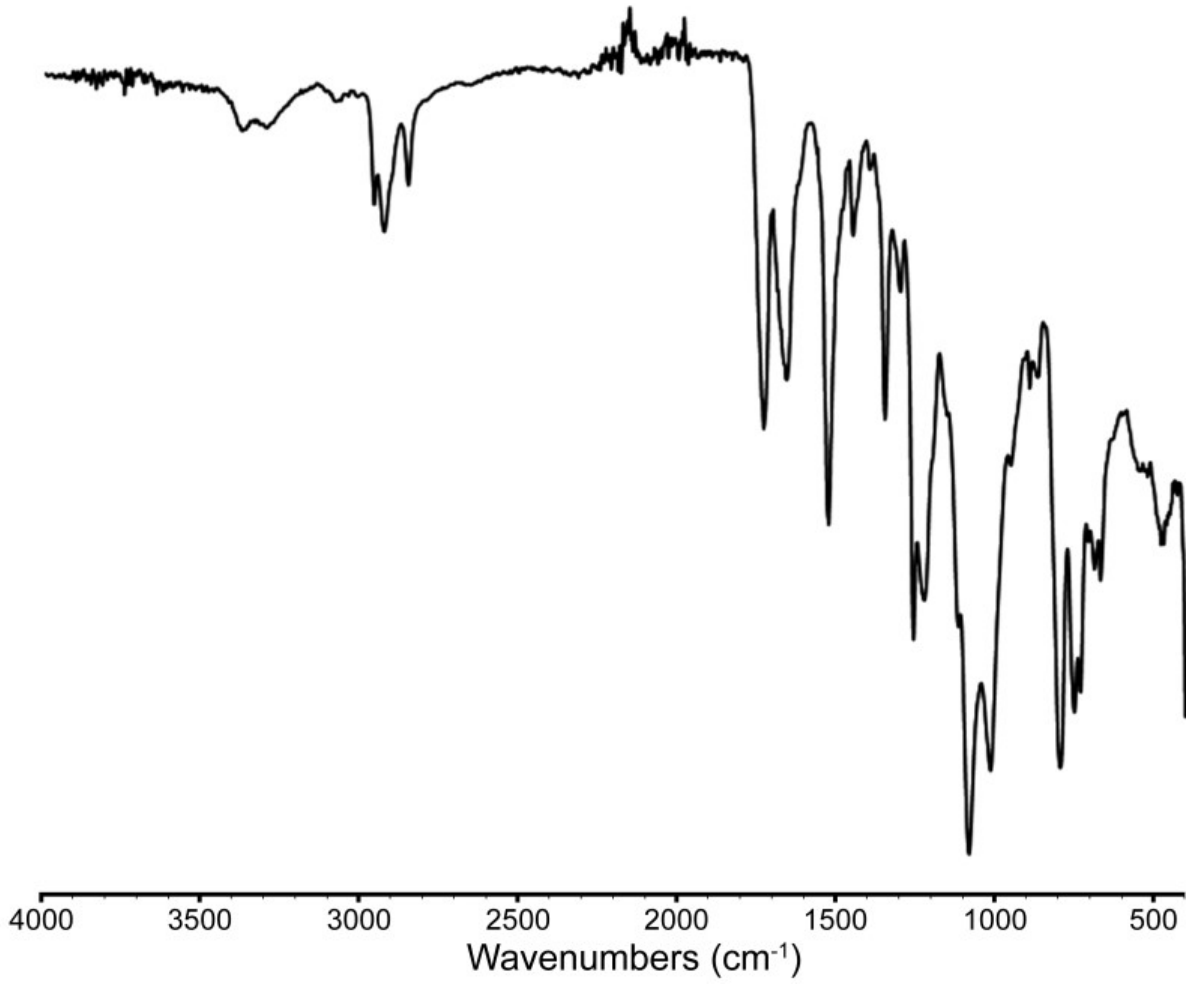

Fig. S16. FT-IR spectrum of **P6**.

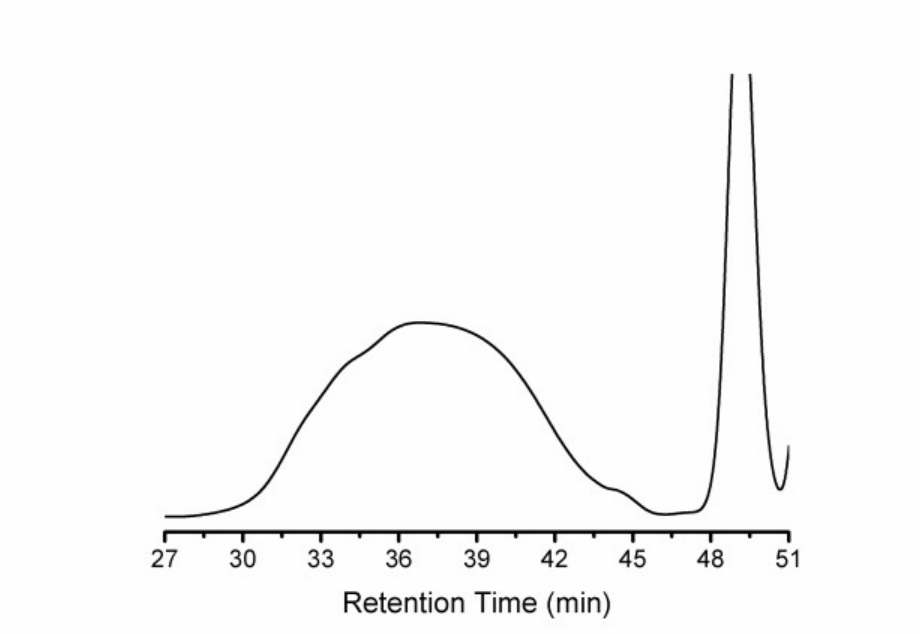

Fig. S17. GPC trace of **P6**.

Synthesis of P7

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), PEG_{400} (367 mg, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.75 mmol, 3 equiv) and CHI (342 µL, 2.75 mmol, 3 equiv) were used. The resulting white sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 978 mg, 95%). ^{1}H NMR ($CDCl_3$, δ) 8.32-7.57 (m, 10H, Ar*H*), 7.12-7.06 (br, 2H, N*H*), 6.34 (s, 2H, OC*H*C=O), 4.52-4.37 (m, 4H, C=OOCH_2), 3.80-3.61 (m, 34H, NHC*H* and OCH_2 of PEG_{400}), 2.03-1.15 (m, 20H, CH_2 of cyclohexane); ^{13}C NMR ($CDCl_3$, δ) 165.76, 163.95, 148.11, 136.78, 133.78, 130.90, 129.86, 123.97, 122.17, 76.40, 67.98, 60.76, 48.92, 32.59, 25.61, 25.33, 24.75.

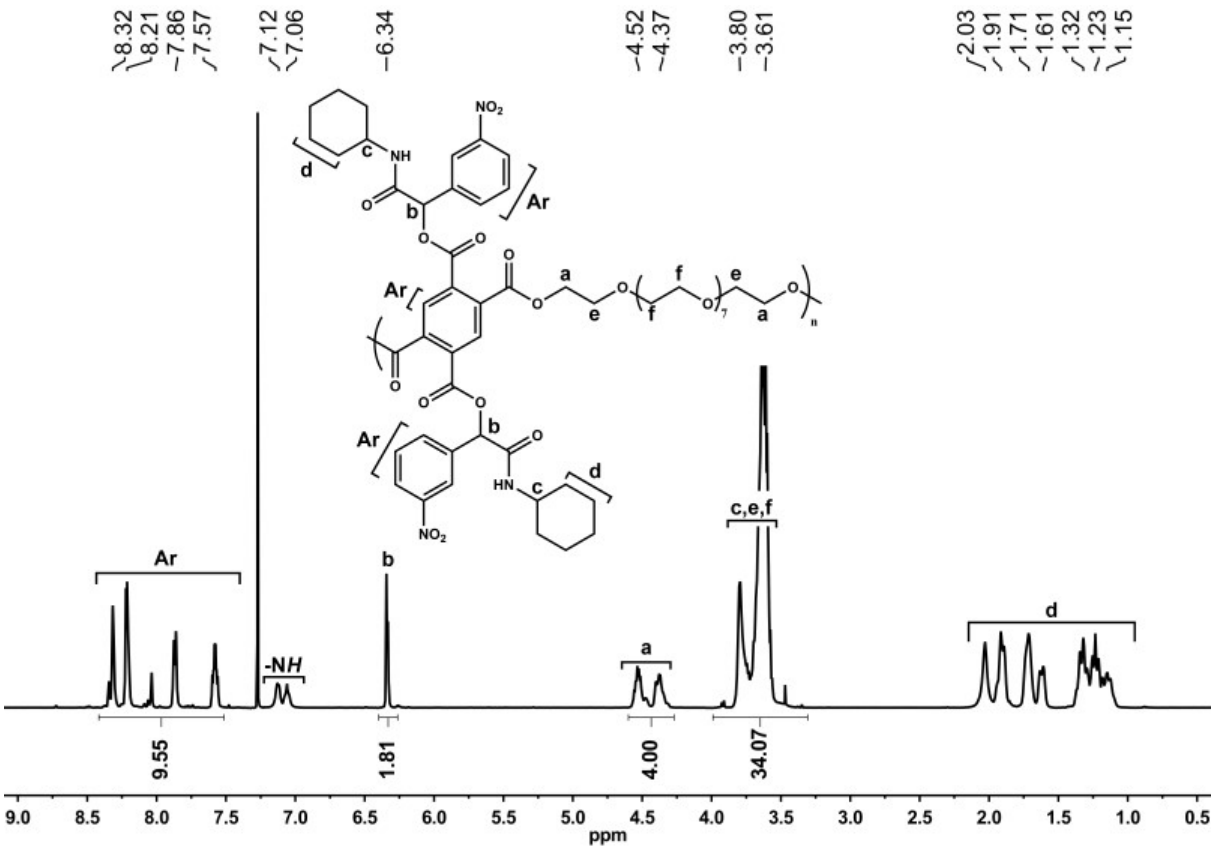

Fig. S18. ^{1}H NMR spectrum of **P7** in $CDCl_3$ (500 MHz).

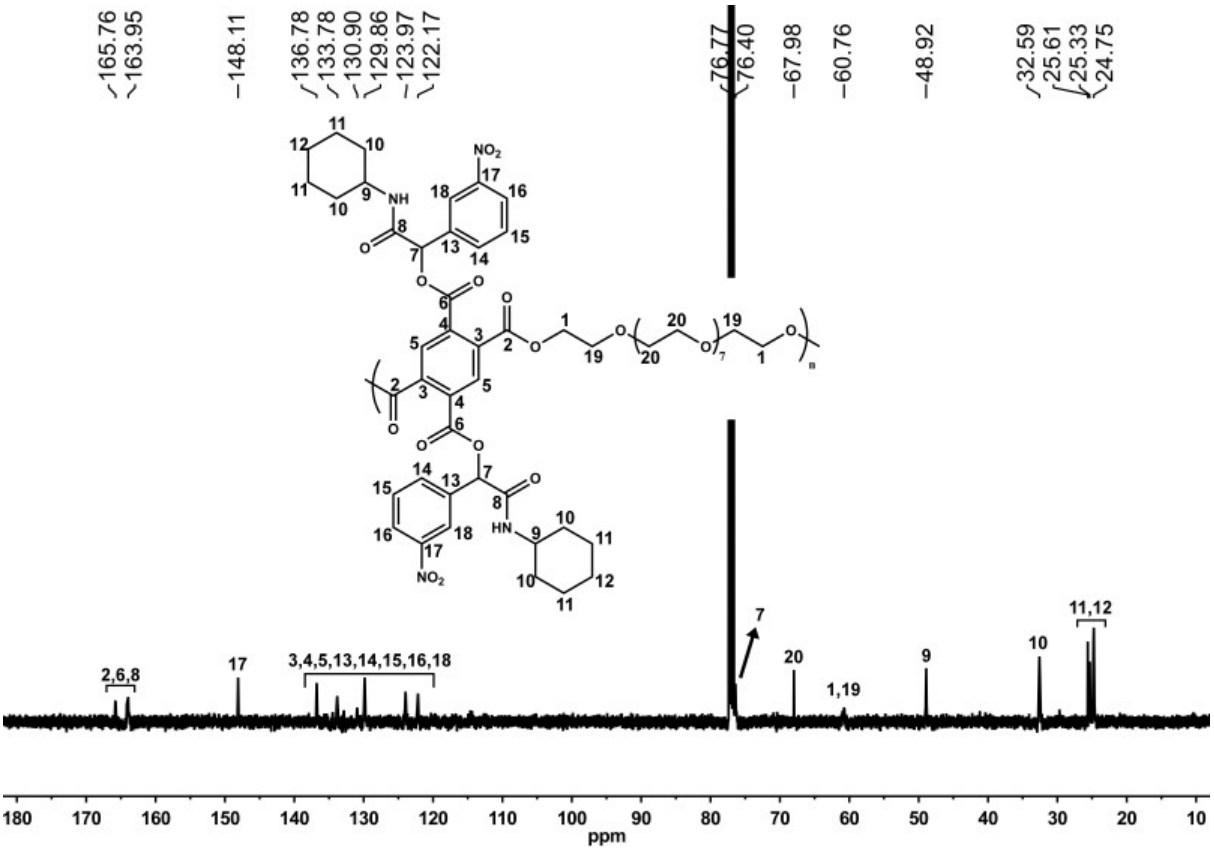

Fig. S19. ^{13}C NMR spectrum of **P7** in $CDCl_3$ (125 MHz).

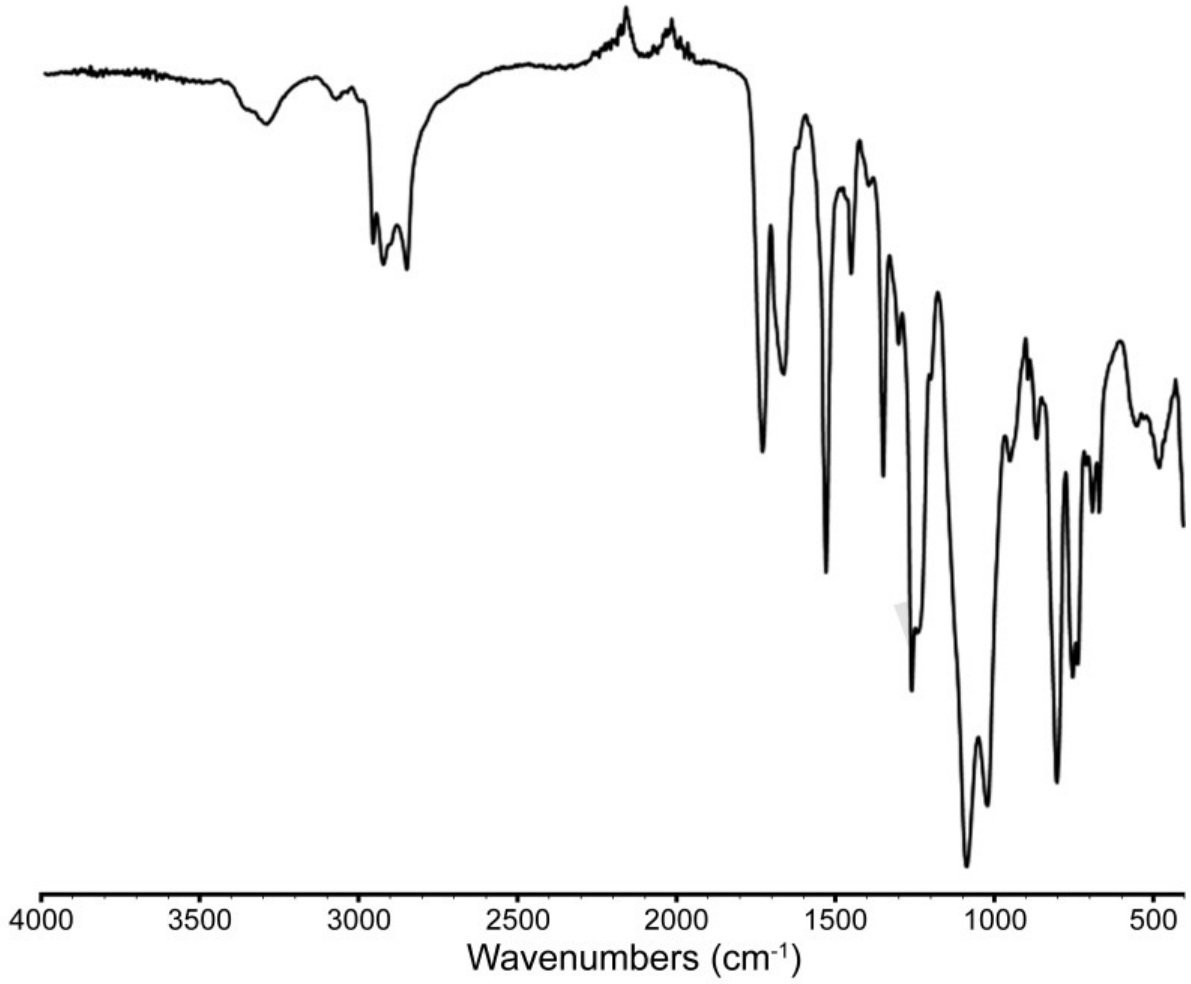

Fig. S20. FT-IR spectrum of **P7**.

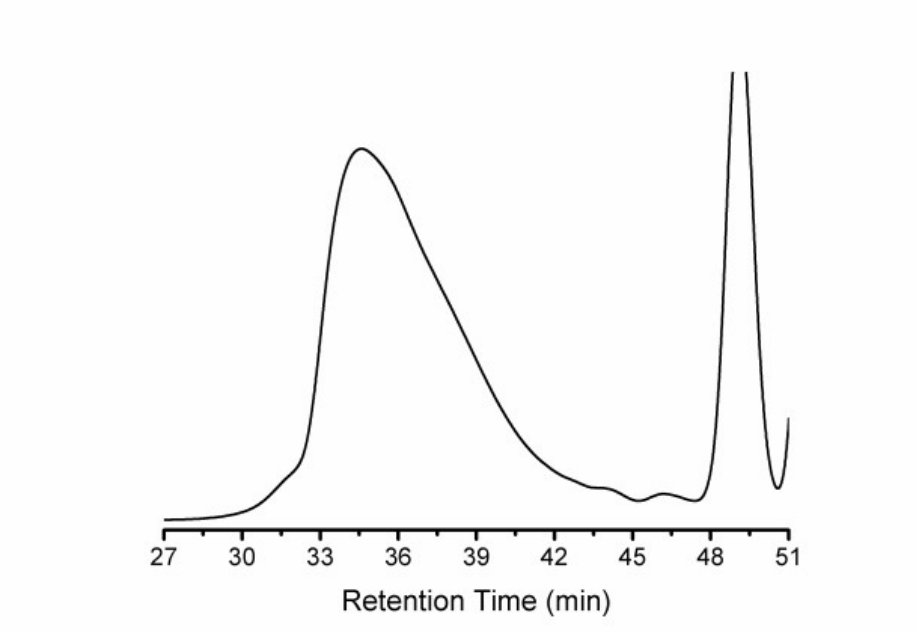

Fig. S21. GPC trace of **P7**.

Synthesis of P8

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), bis(2-hydroxyethyl) disulfide (123 µL, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.75 mmol, 3 equiv) and CHI (342 µL, 2.75 mmol, 3 equiv) were used. The resulting white sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 792 mg, 95%). ^{1}H NMR ($CDCl_3$, δ) 8.29-7.55 (m, 10H, Ar*H*), 7.11 (br, 2H, N*H*), 6.33 (s, 2H, OC*H*C=O), 4.64-4.56 (d, 4H, C=OOCH_2), 3.76 (br, 2H, NHC*H*), 3.02 (br, 4H, CH_2S-S), 1.89-1.11 (m, 20H, CH_2 of cyclohexane); ^{13}C NMR ($CDCl_3$, δ) 165.84, 165.36, 164.40, 148.17, 137.00, 134.42, 133.92, 133.40, 130.90, 129.89,123.98, 121.97, 121.96, 76.30, 64.41, 48.89, 36.32, 32.59, 25.41, 24.84.

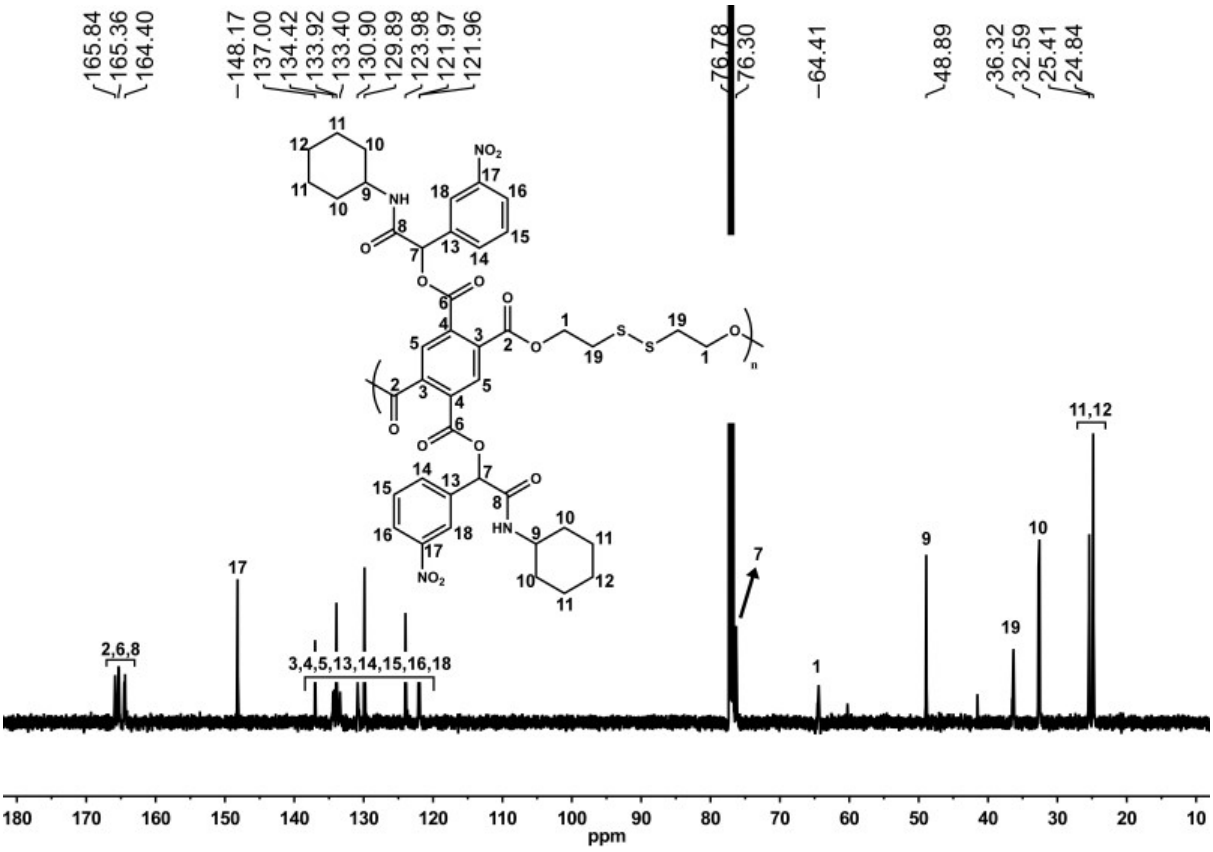

Fig. S22. ^{13}C NMR spectrum of **P8** in $CDCl_3$ (125 MHz).

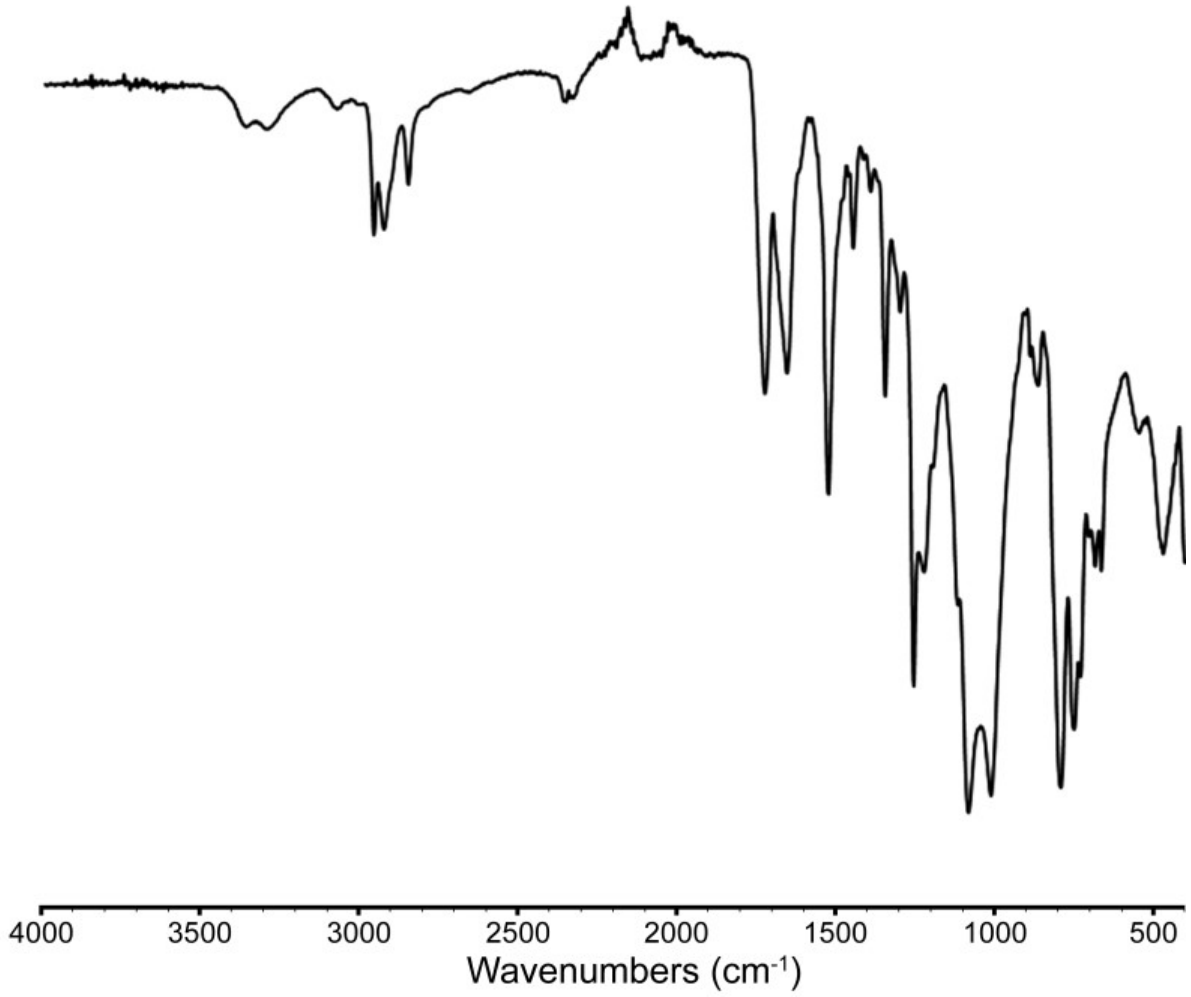

Fig. S23. FT-IR spectrum of **P8**.

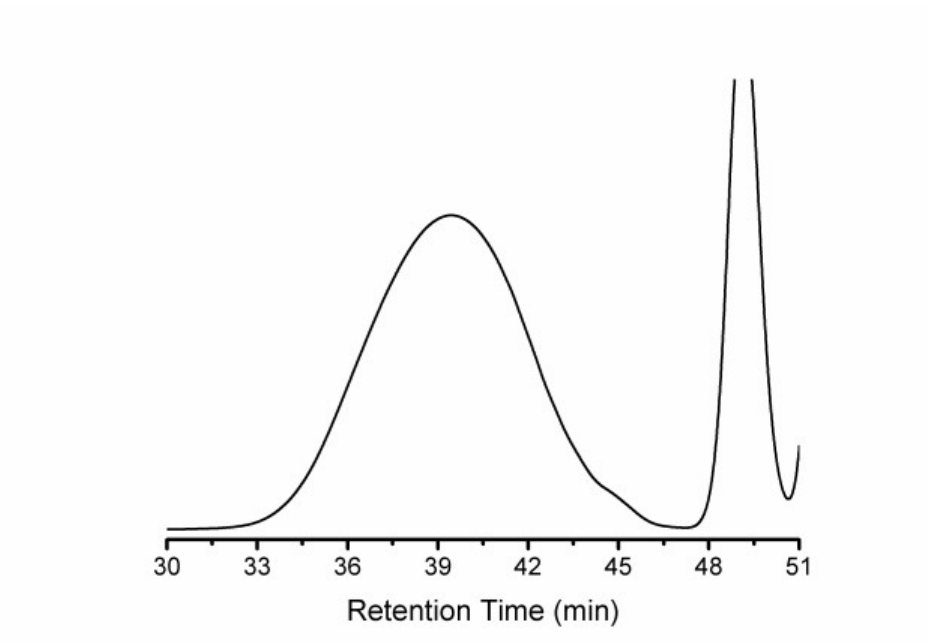

Fig. S24. GPC trace of **P8**.

Synthesis of P9

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), 2,2-bis(bromomethyl)-1,3-propanediol (240 mg, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.75 mmol, 3 equiv) and CHI (342 μL, 2.75 mmol, 3 equiv) were employed. The resulting white solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 438 mg, 48%). ^{1}H NMR ($CDCl_3$, δ) 8.28-7.53 (m, 10H, Ar*H*), 6.99 (br, 2H, N*H*), 6.30 (br, 2H, OC*H*C=O), 4.47 (br, 4H, C=OOCH_2), 3.72-3.57 (m, 6H, NHC*H* and CCH_2Br), 2.00-1.13 (m, 20H, CH_2 of cyclohexane); ^{13}C NMR ($CDCl_3$, δ) 165.71, 164.89, 164.23, 148.05, 136.79, 133.79, 129.99, 124.03, 122.33, 109.99, 76.16, 65.27, 50.84, 48.99, 42.73, 33.38, 32.56, 25.34, 24.84.

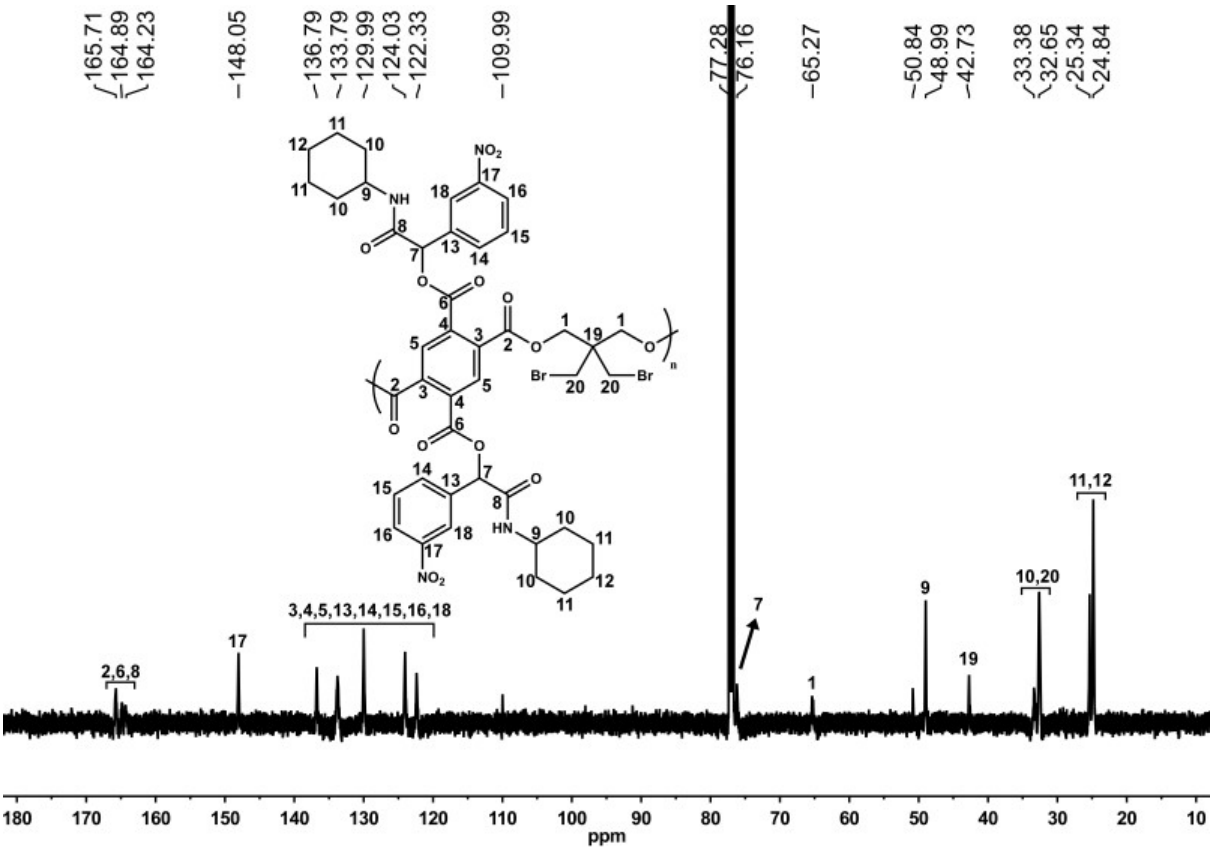

Fig. S25. ^{13}C NMR spectrum of **P9** in $CDCl_3$ (125 MHz).

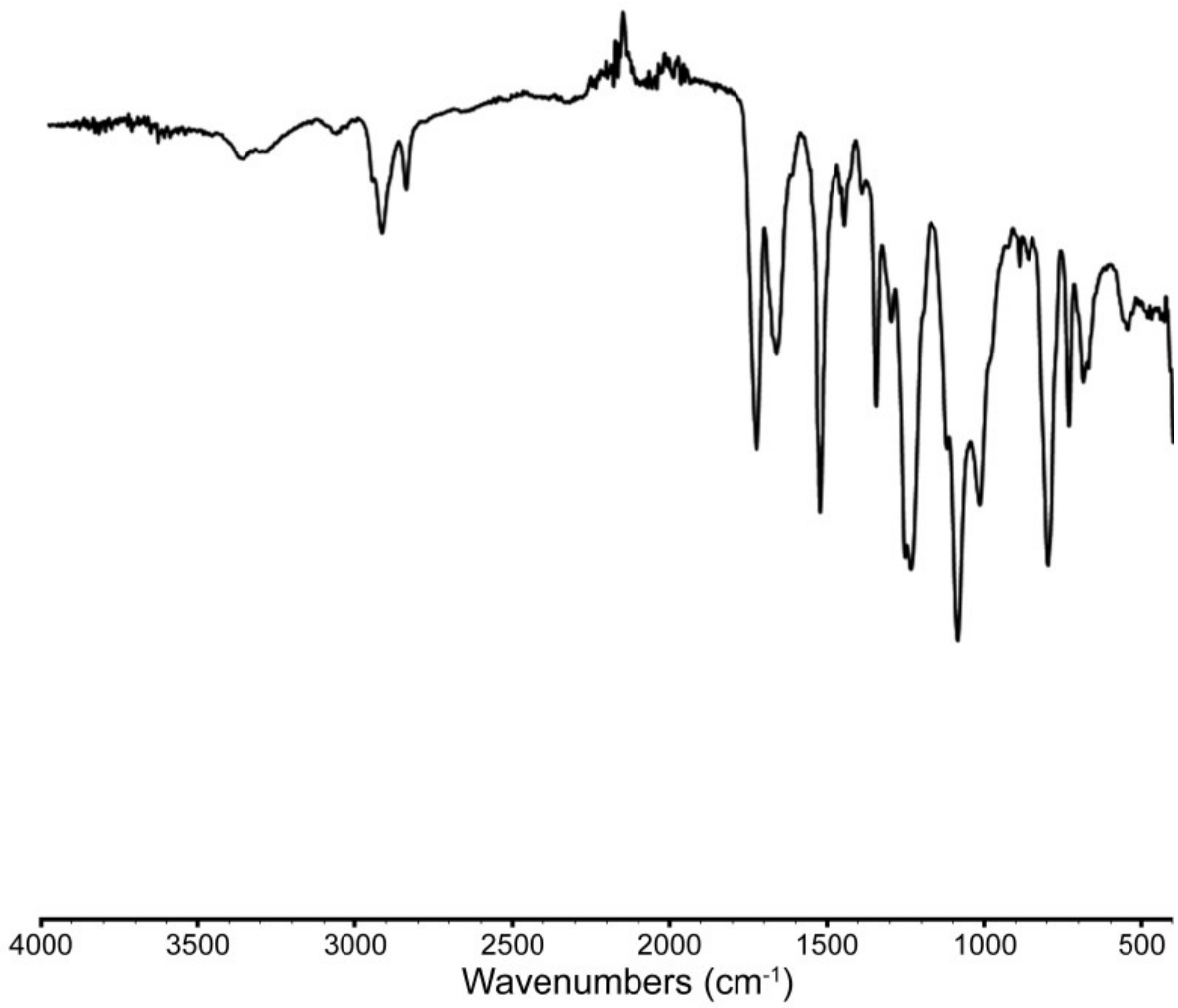

Fig. S26. FT-IR spectrum of **P9**.

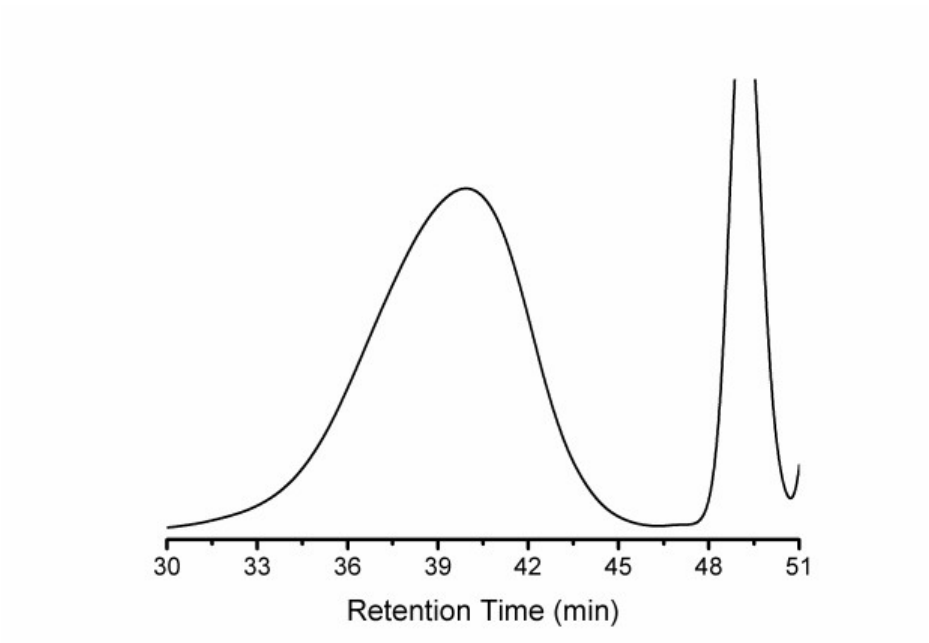

Fig. S27. GPC trace of **P9**.

Synthesis of P10

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), 2-azidoethyl-3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (186 mg, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.75 mmol, 3 equiv) and CHI (342 µL, 2.75 mmol, 3 equiv) were used. The resulting pale yellow sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 565 mg, 65%). ^{1}H NMR ($CDCl_3$, δ) 8.30-7.54 (m, 10H, Ar*H*), 7.01 (br, 2H, N*H*), 6.32 (br, 2H, OC*H*C=O), 4.55-4.30 (m, 6H, C=OOC$H_2$and C=OOCH_2CH$_2$N$_3$), 3.70 (br, 2H, NHC*H*), 3.44 (br, 2H, C=OOCH$_2$CH_2N$_3$), 2.18-1.12 (m, 23H, CH_2 of cyclohexane and CCH_3); ^{13}C NMR ($CDCl_3$, δ) 171.80, 165.87, 165.01, 164.38, 148.12, 136.89, 133.78, 129.91, 123.95, 122.23, 76.16, 64.27, 48.91, 48.89, 46.35, 32.57, 25.32, 24.80, 17.80.

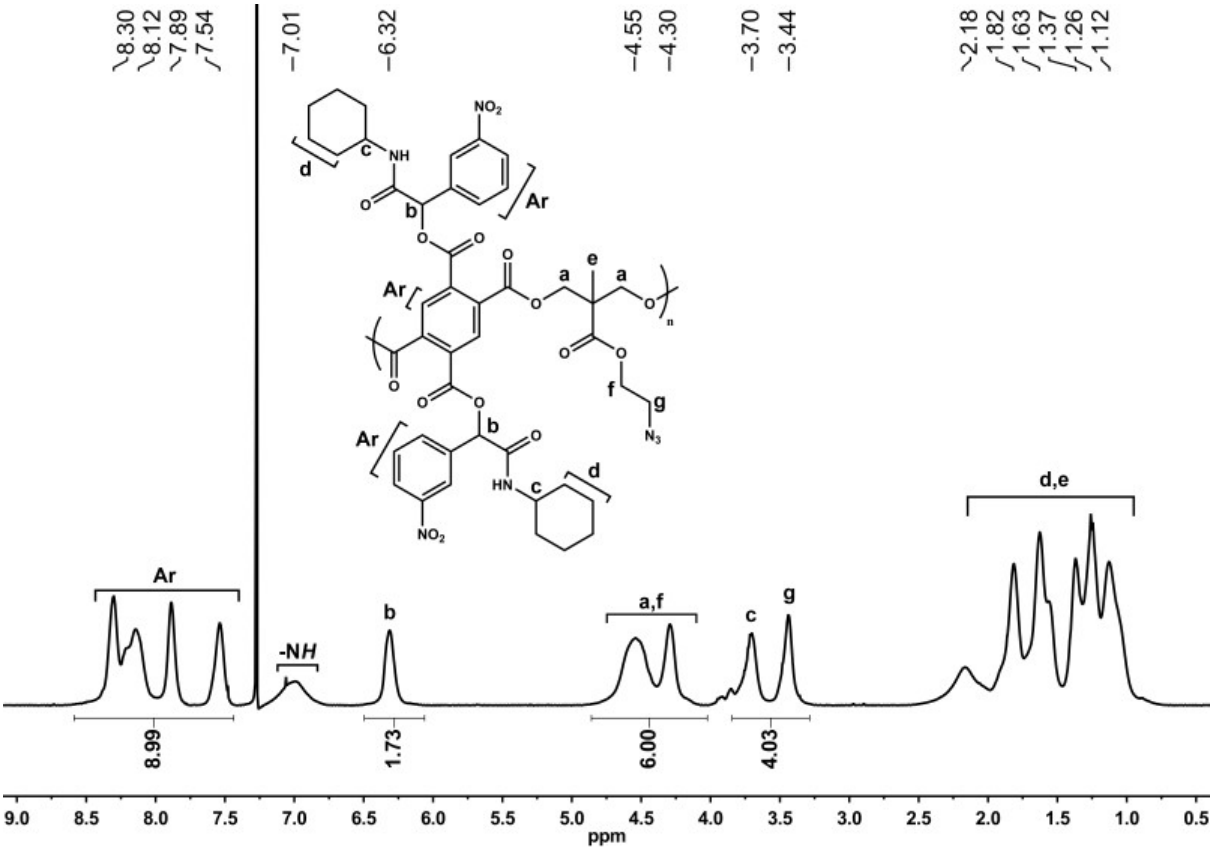

Fig. S28. ^{1}H NMR spectrum of **P10** in $CDCl_3$ (500 MHz).

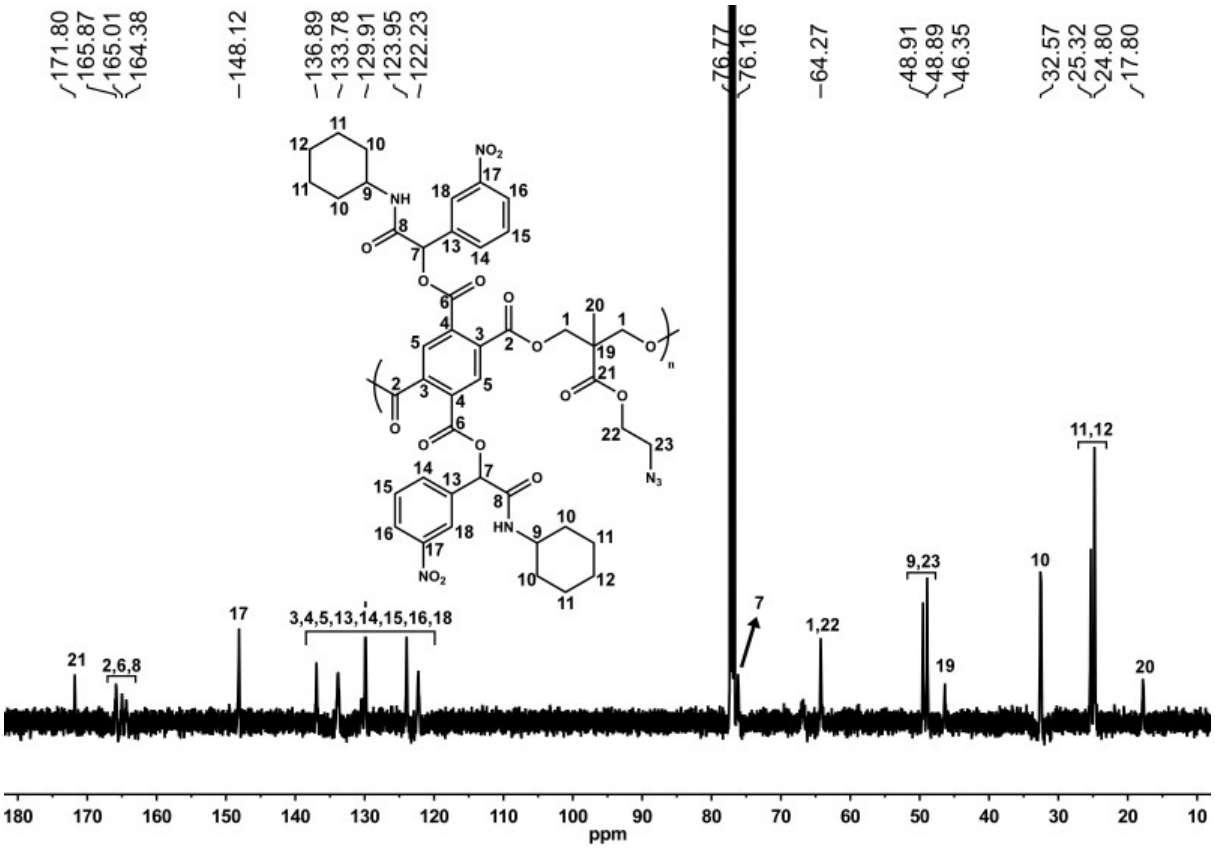

Fig. S29. ^{13}C NMR spectrum of **P10** in $CDCl_3$ (125 MHz).

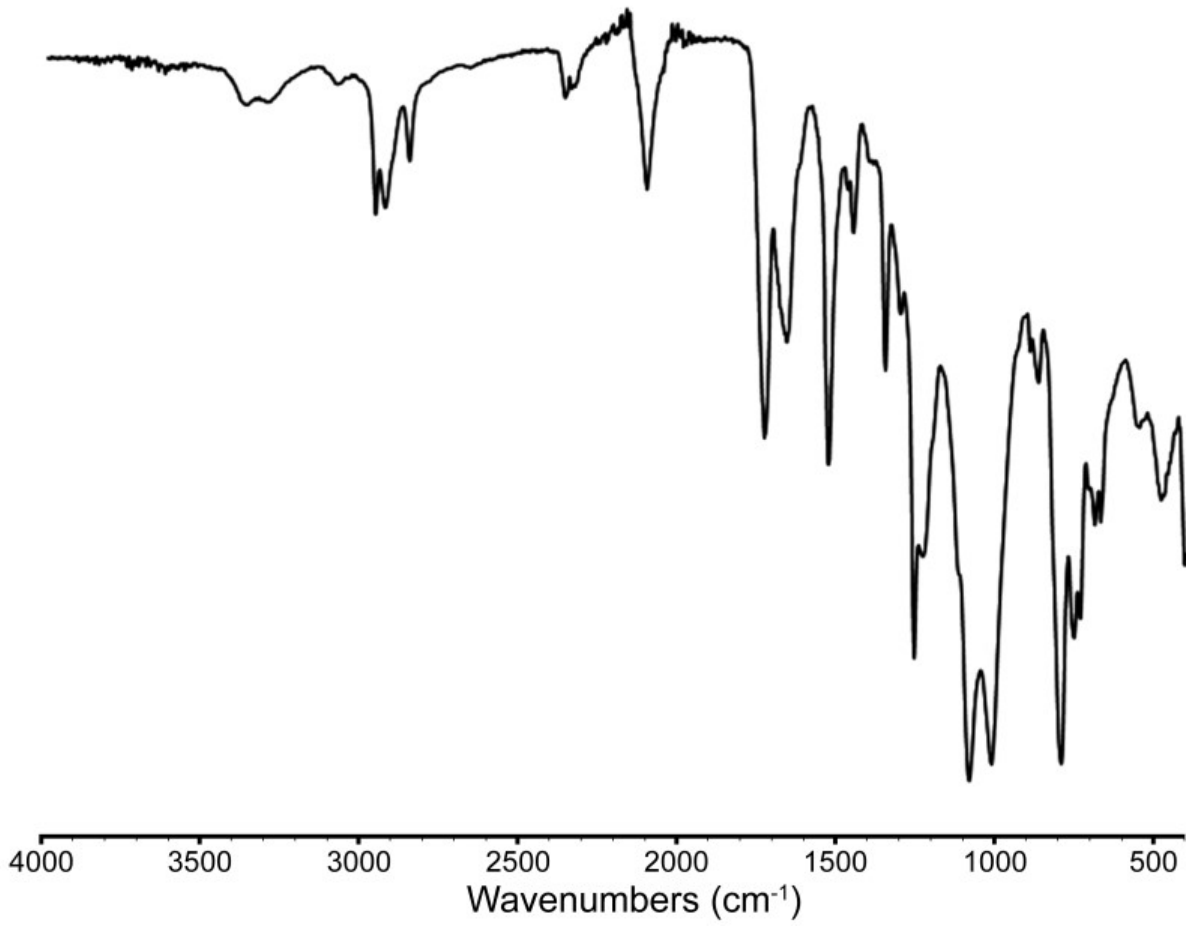

Fig. S30. FT-IR spectrum of **P10**.

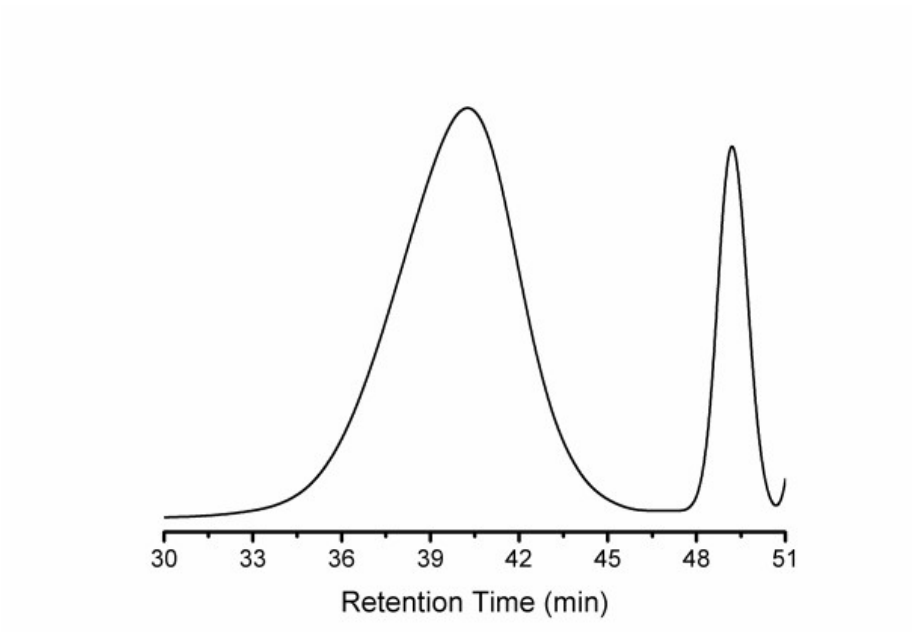

Fig. S31. GPC trace of **P10**.

Synthesis of P11

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv) and 4,8-bis(hydroxymethyl)tricyclo[5.2.1.$0^{2,6}$]decane (180 mg, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.75 mmol, 3 equiv) and CHI (342 μL, 2.75 mmol, 3 equiv) were used. The resulting white solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 699 mg, 82%). ^{1}H NMR ($CDCl_3$, δ) 8.28-7.55 (m, 10H, Ar*H*), 7.14 (br, 2H, N*H*), 6.34 (br, 2H, OC*H*C=O), 4.17 (br, 4H, C=OOCH_2), 3.76 (br, 2H, NHC*H*), 2.49-1.11 (m, 34H, aliphatic C*H* and CH_2 protons); ^{13}C NMR ($CDCl_3$, δ) 165.78, 164.60, 148.22, 137.10, 133.90, 130.71, 129.76, 123.88, 121.91, 76.23, 70.41, 48.87, 44.46, 41.39, 40.26, 38.73, 33.29, 32.75, 32.58, 25.45, 24.86.

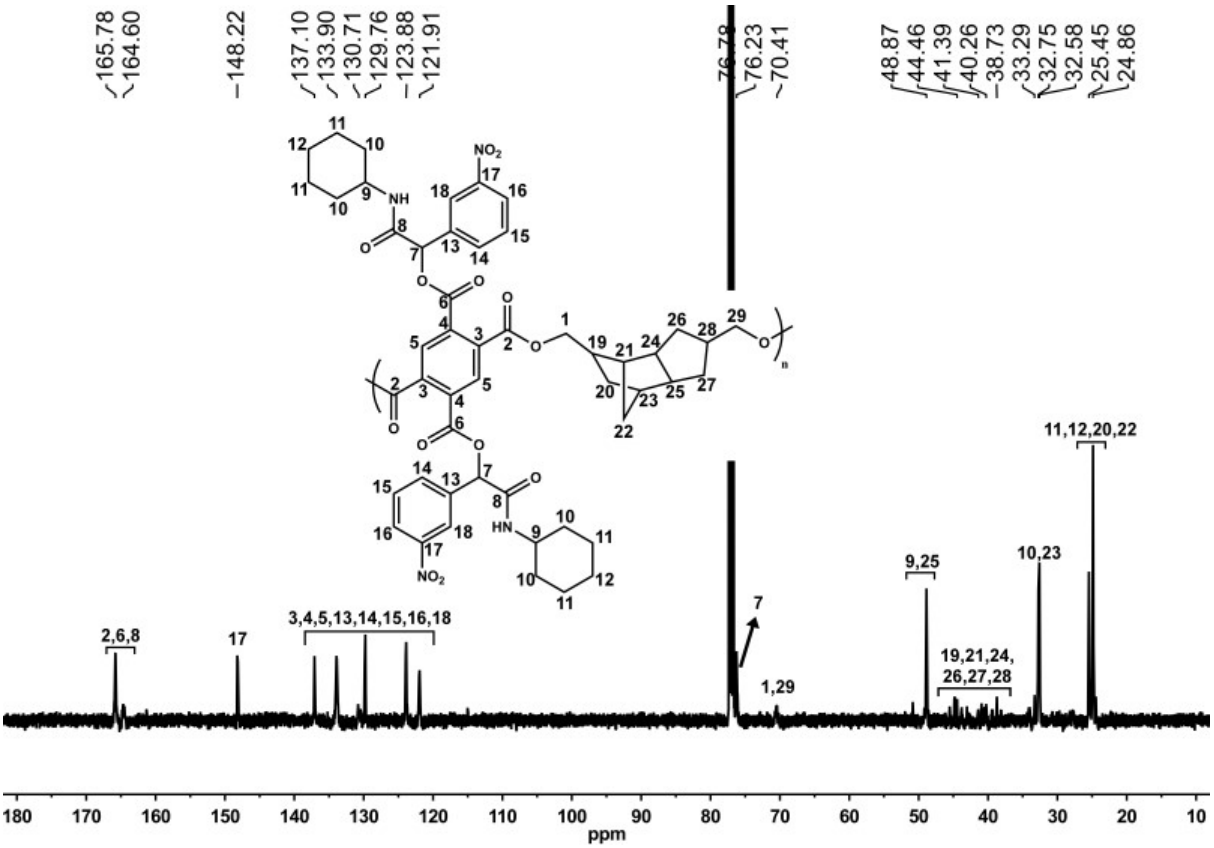

Fig. S32. ^{13}C NMR spectrum of **P11** in $CDCl_3$ (125 MHz).

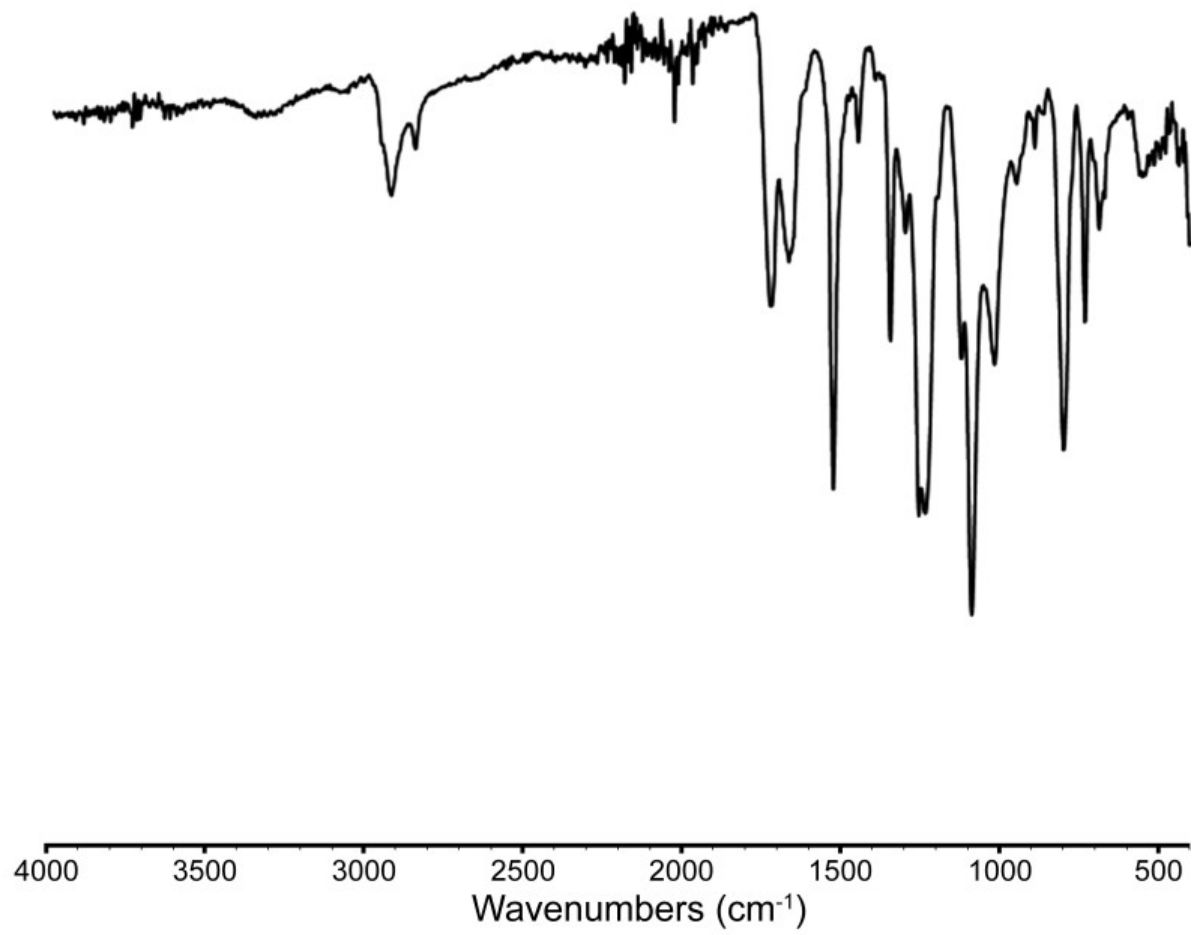

Fig. S33. FT-IR spectrum of **P11**.

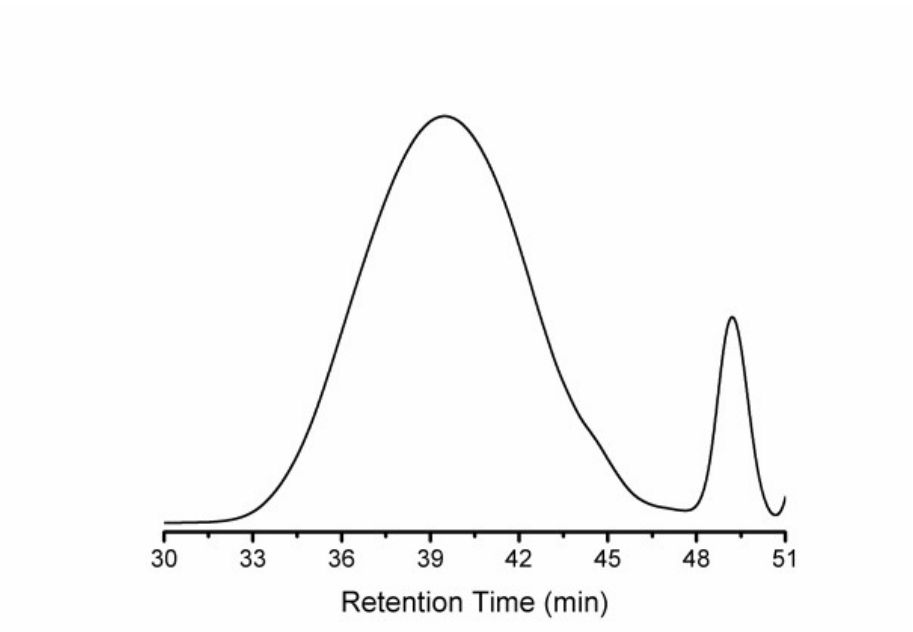

Fig. S34. GPC trace of **P11**.

Synthesis of P12

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), 2,5-hexanediol (108 mg, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.75 mmol, 3 equiv) and CHI (342 µL, 2.75 mmol, 3 equiv) were employed. The resulting white sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 212 mg, 27%). ^{1}H NMR ($CDCl_3$, δ) 8.29-7.23 (m, 10H, Ar*H*), 7.10 (br, 2H, N*H*), 6.33 (br, 2H, OC*H*C=O), 5.13 (br, 2H, C=OOC*H*CH_3), 3.77 (br, 2H, NHC*H*), 1.88-1.10 (m, 30H, CH_2 of cyclohexane, CH_2 and CH_3 of 2,5-hexanediol); ^{13}C NMR ($CDCl_3$, δ) 174.50, 165.95, 165.15, 148.15, 137.03, 133.85, 129.74, 123.96, 122.20, 76.11, 73.76, 48.87, 32.57, 31.19, 29.70, 25.42, 24.83, 19.54.

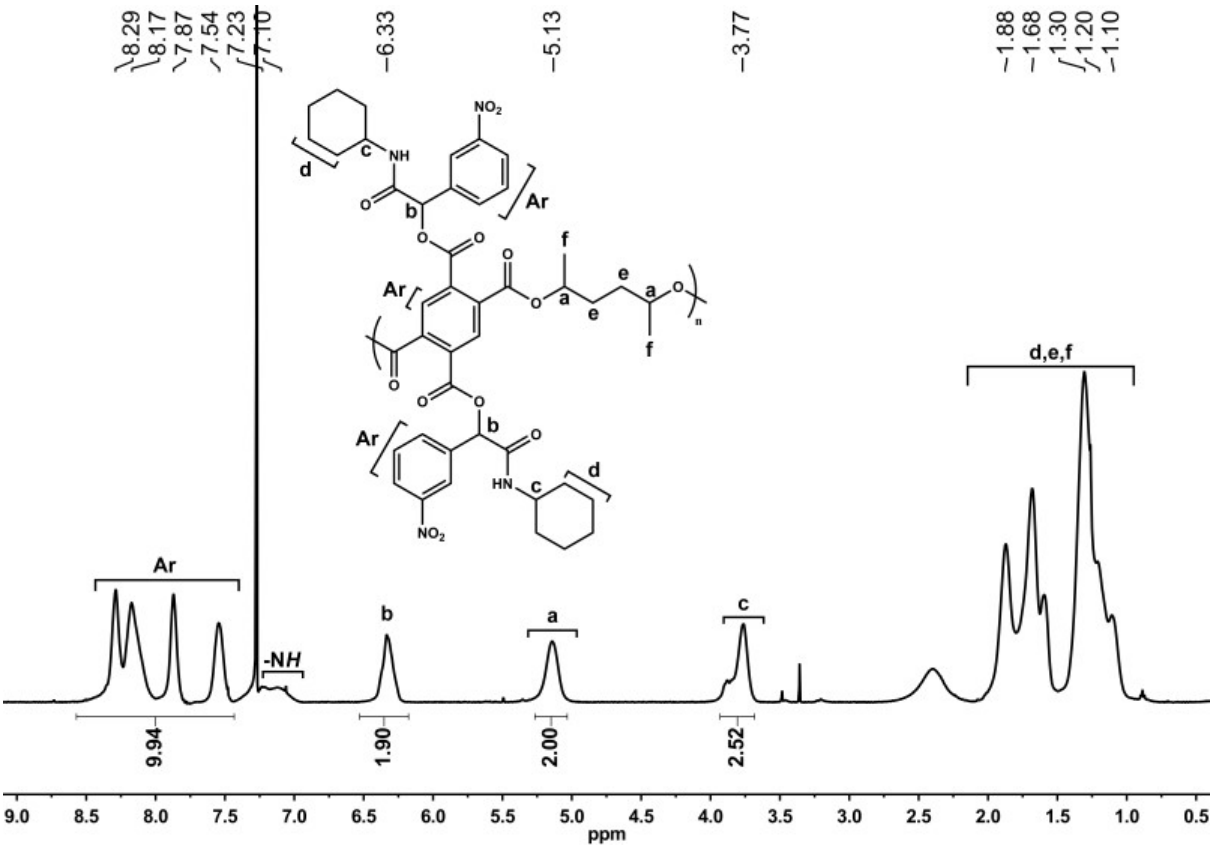

Fig. S35. ^{1}H NMR spectrum of **P12** in $CDCl_3$ (500 MHz).

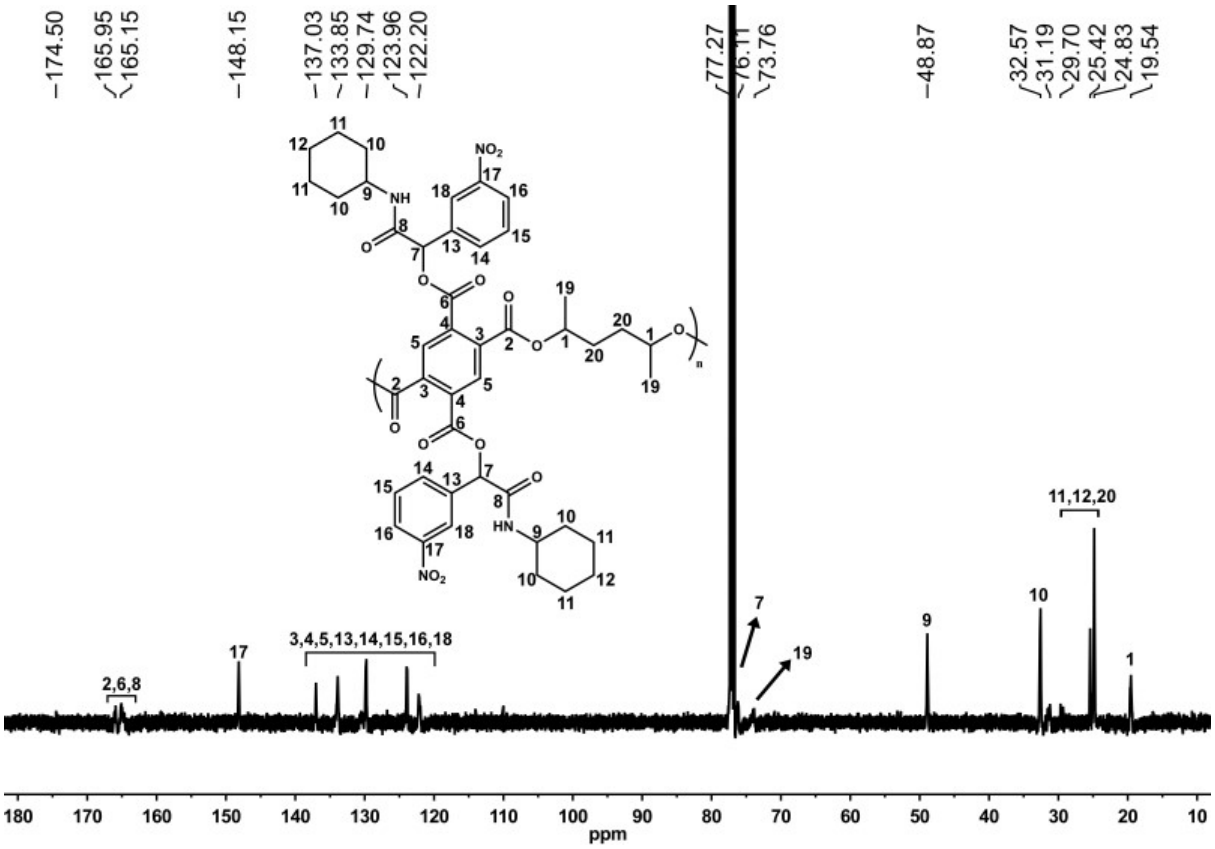

Fig. S36. ^{13}C NMR spectrum of **P12** in $CDCl_3$ (125 MHz).

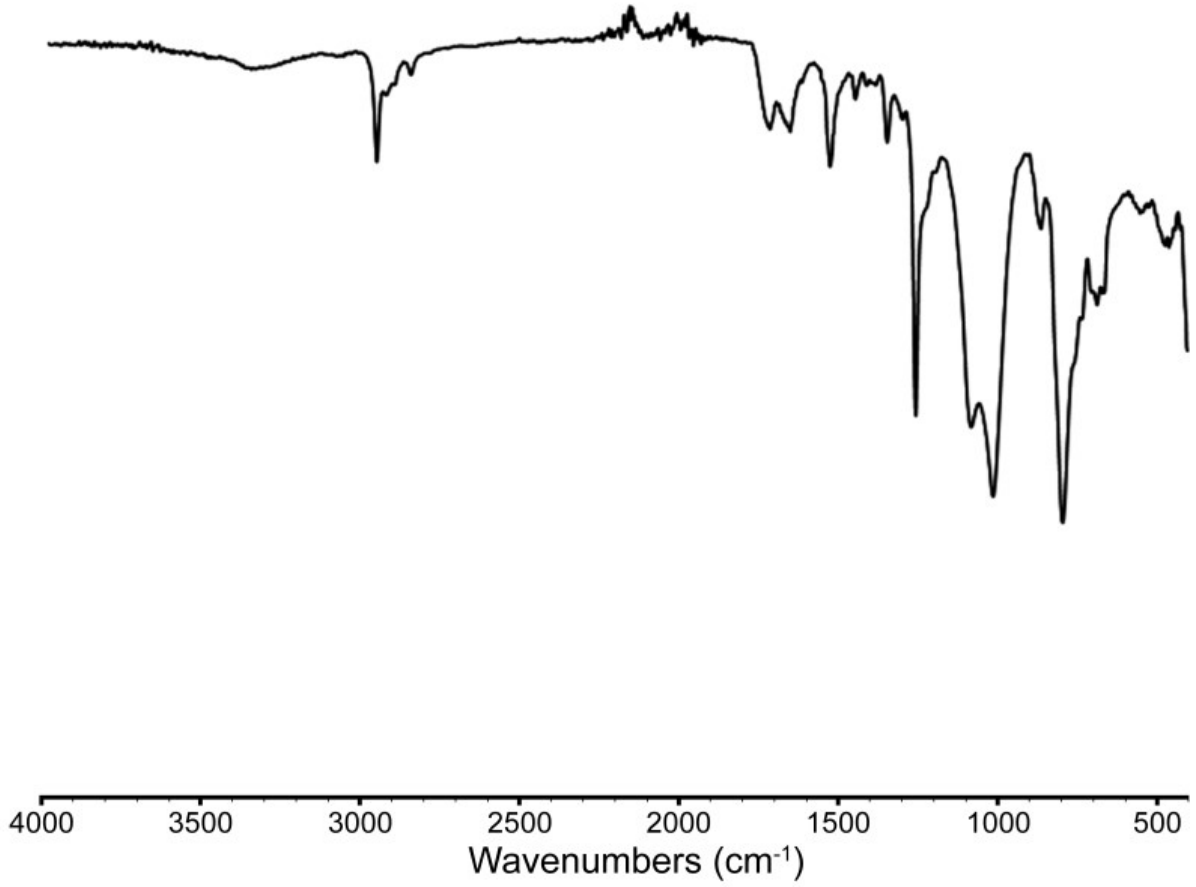

Fig. S37. FT-IR spectrum of **P12**.

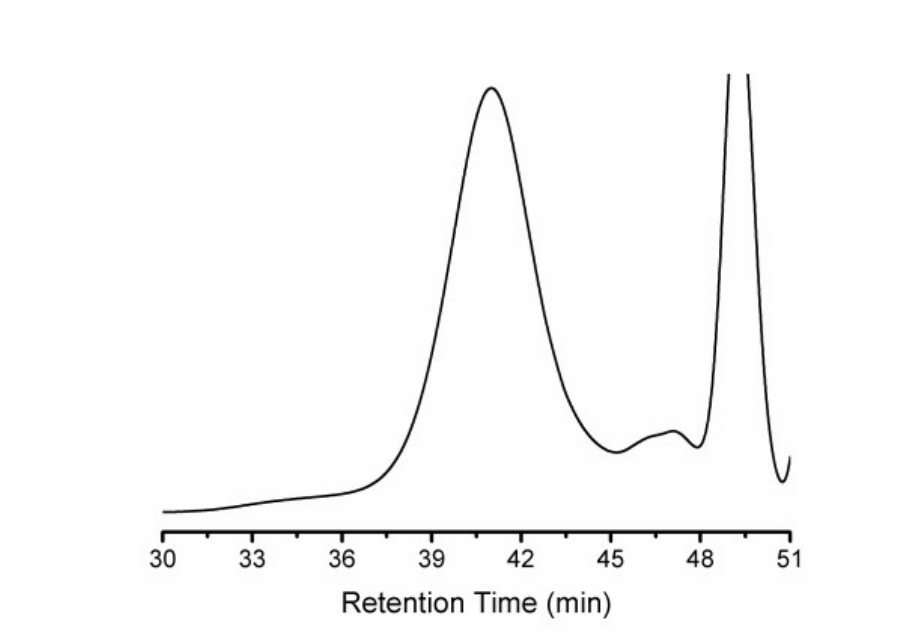

Fig. S38. GPC trace of **P12**.

Synthesis of P13

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv) and 3,4-bis(hydroxymethyl)furan (115 mg, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.75 mmol, 3 equiv) and CHI (342 μL, 2.75 mmol, 3 equiv) were used. The resulting white sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 374 mg, 47%). ^{1}H NMR ($CDCl_3$, δ) 8.26-7.48 (m, 12H, Ar*H* and C*H* of furan), 7.10 (br, 2H, N*H*), 6.26 (br, 2H, OC*H*C=O), 5.23 (br, 4H, C=OOCH_2), 3.72 (br, 2H, NHC*H*), 1.83-1.14 (m, 20H, CH_2 of cyclohexane); ^{13}C NMR ($CDCl_3$, δ) 166.00, 165.07, 164.48, 148.03, 143.51, 136.96, 133.68, 129.82, 123.84, 122.02, 118.72, 76.20, 58.50, 48.89, 32.63, 25.34, 24.78.

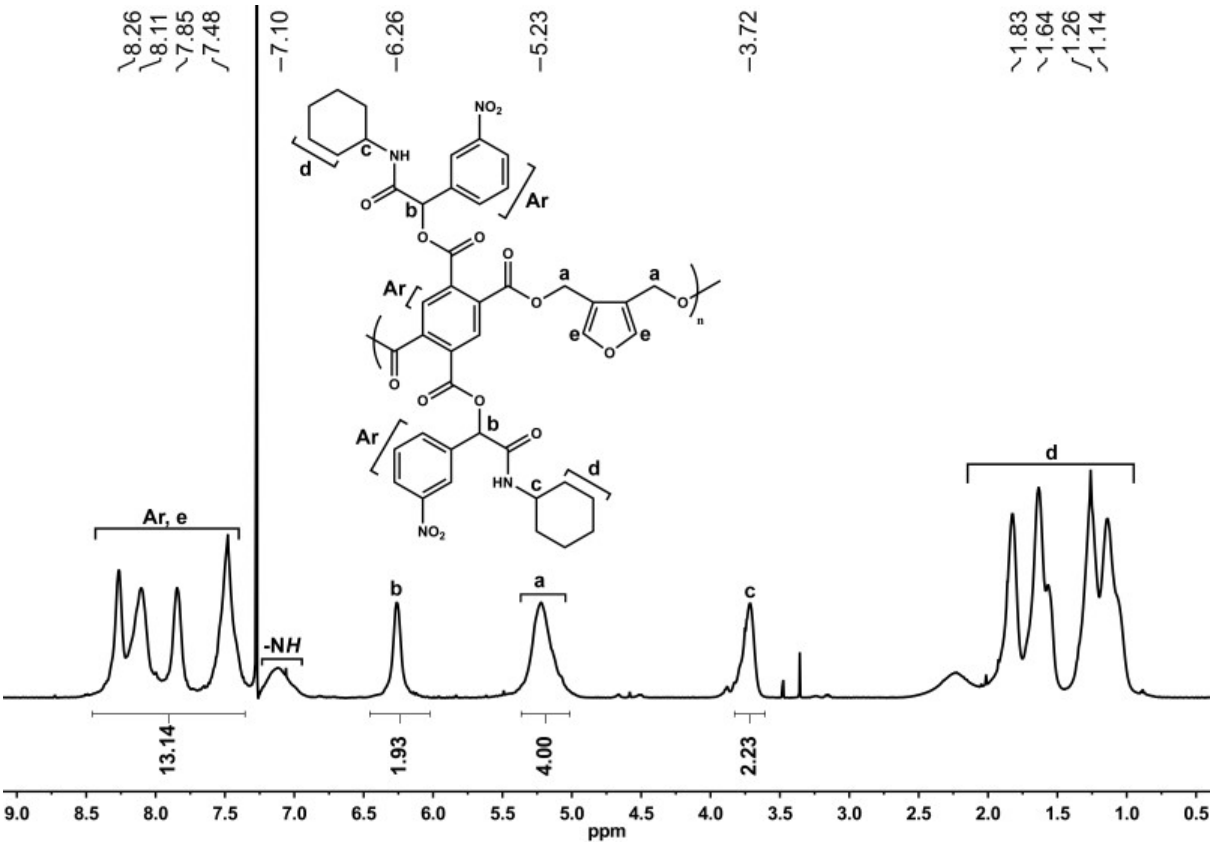

Fig. S39. ^{1}H NMR spectrum of **P13** in $CDCl_3$ (500 MHz).

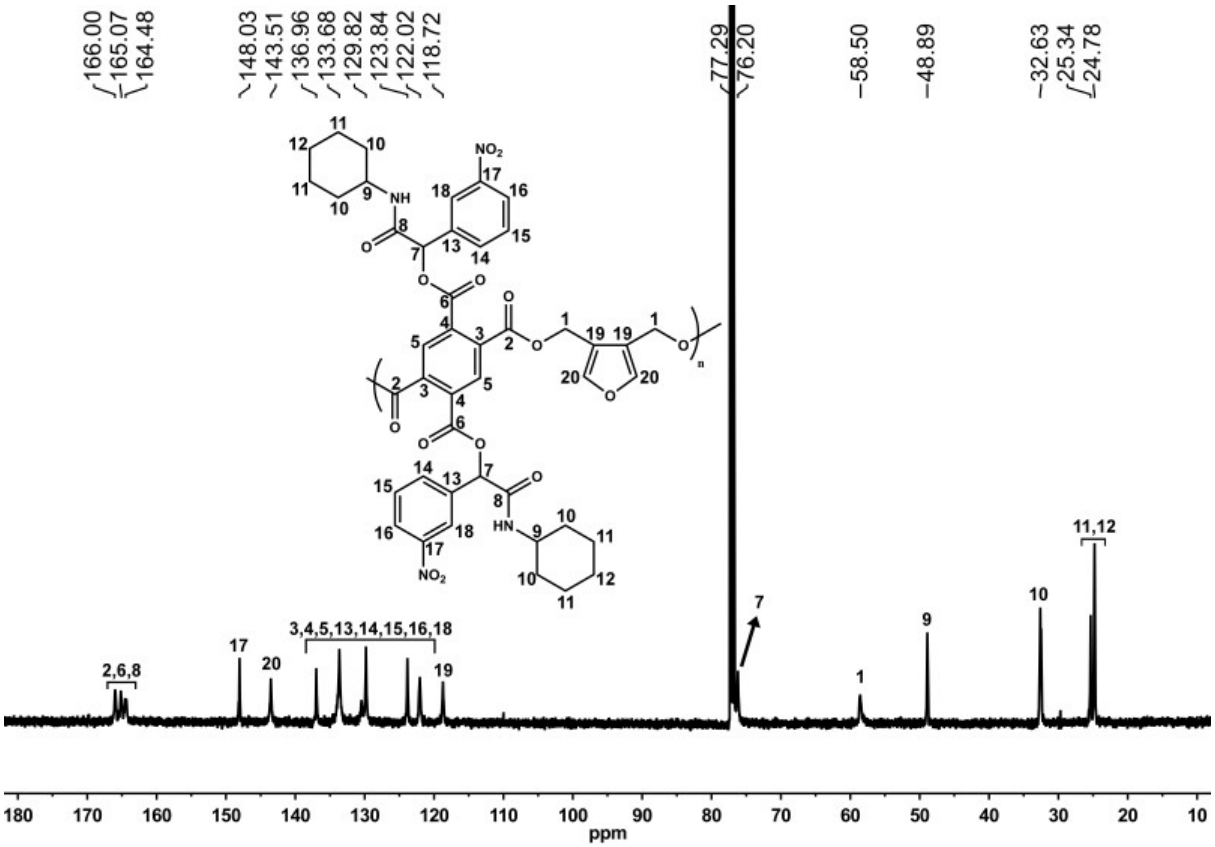

Fig. S40. ^{13}C NMR spectrum of **P13** in $CDCl_3$ (125 MHz).

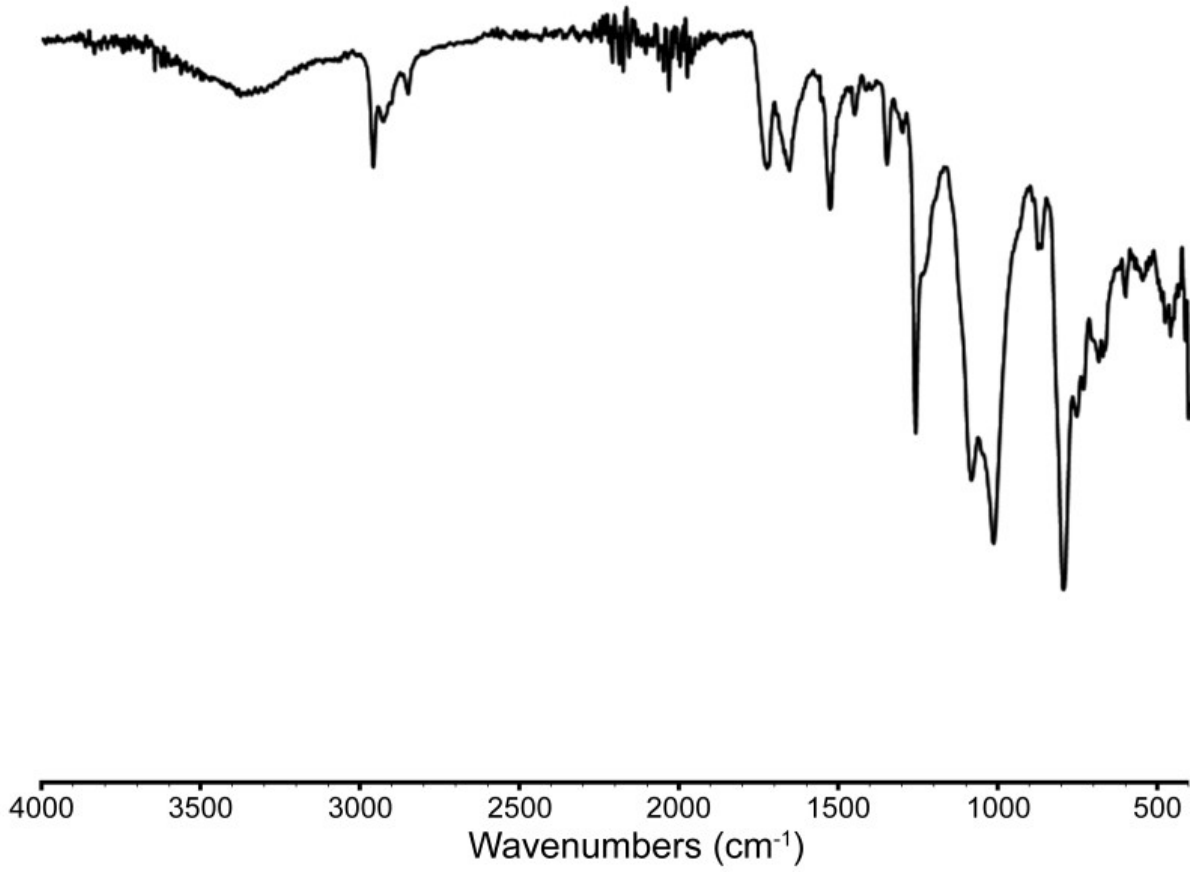

Fig. S41. FT-IR spectrum of **P13**.

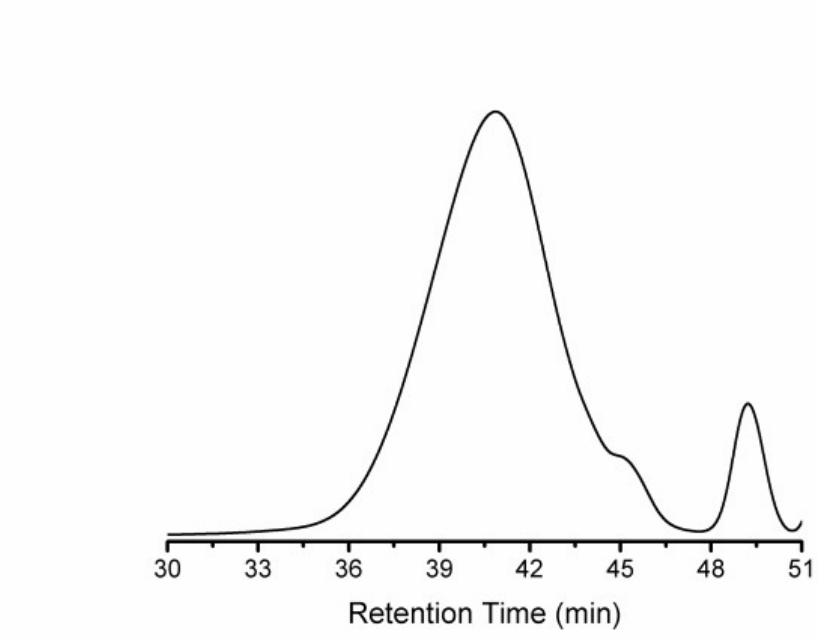

Fig. S42. GPC trace of **P13**.

Synthesis of P14

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), 1,4-butanediol (82.6 mg, 0.920 mmol, 1 equiv), isobutyraldehyde (251 µL, 2.75 mmol, 3 equiv) and CHI (342 µL, 2.75 mmol, 3 equiv) were used. Solution was precipitated into 30 mL of diethyl ether and residual solvent was removed by decantation. The dissolution-precipitation process (THF-diethyl ether) was repeated two times. The resulting white sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 374 mg, 61%). ^{1}H NMR ($CDCl_3$, δ) 8.16 (s, 2H, Ar*H*), 6.79-6.57 (m, 2H, N*H*), 5.18 (br, 2H, OC*H*C=O), 4.40 (d, 4H, C=OOCH_2), 3.80 (br, 2H, NHC*H*), 2.42 (br, 2H, C*H*(CH_3)$_2$), 1.97-0.93 (m, 36H, CH_2 of cyclohexane, C=OOCH$_2$CH_2 and CH(CH_3)$_2$); ^{13}C NMR ($CDCl_3$, δ) 167.40, 165.87, 165.11, 134.92, 134.54, 133.52, 130.69, 129.97, 80.48, 66.05, 48.34, 33.05, 32.68, 31.00, 30.38, 25.55, 24.91, 24.13, 18.94, 16.61.

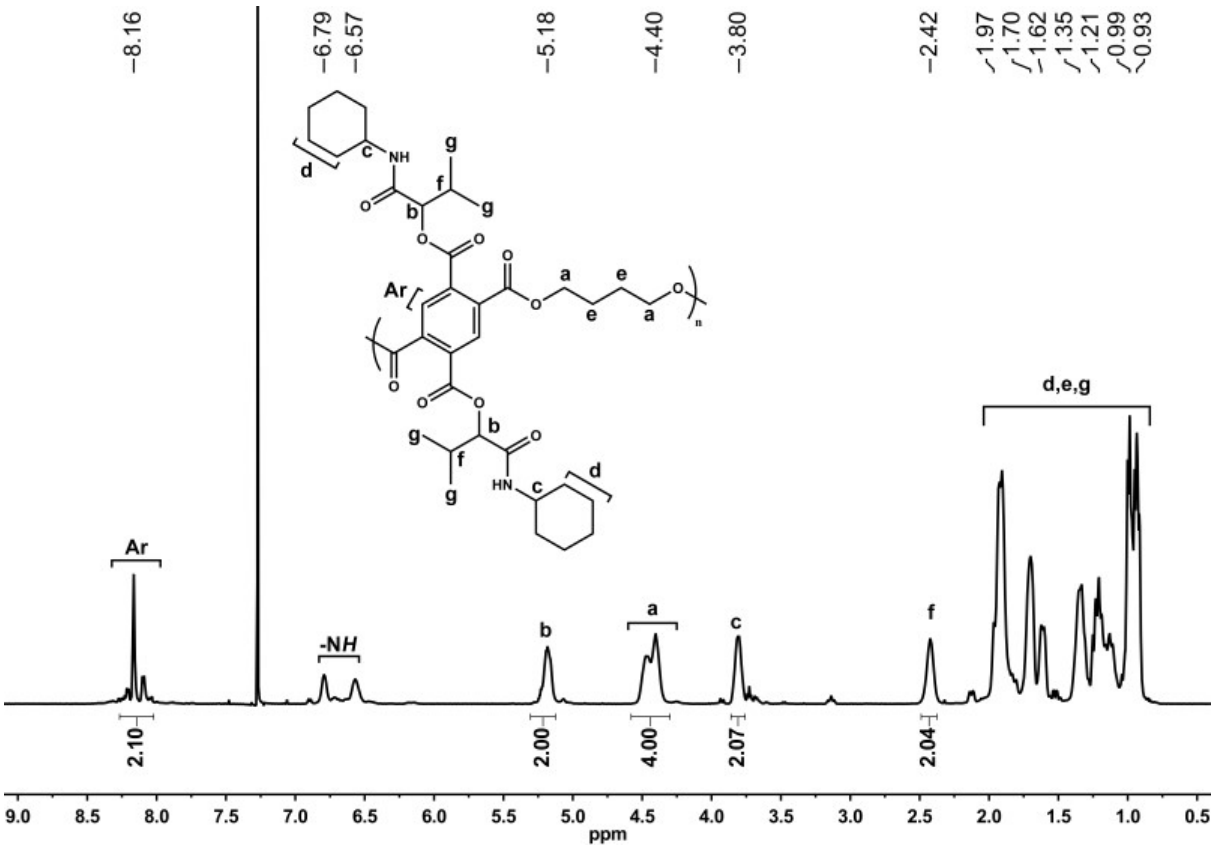

Fig. S43. ^{1}H NMR spectrum of **P14** in $CDCl_3$ (500 MHz).

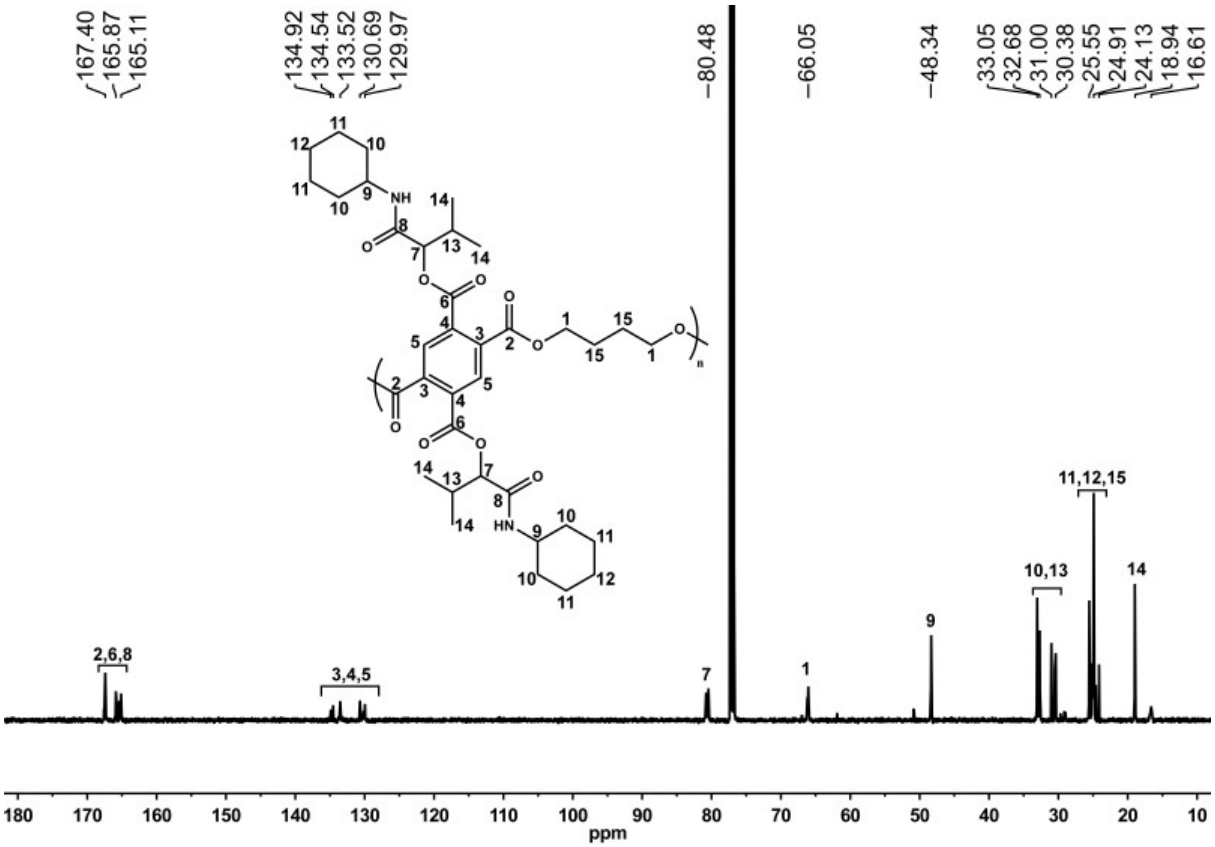

Fig. S44. ^{13}C NMR spectrum of **P14** in $CDCl_3$ (125 MHz).

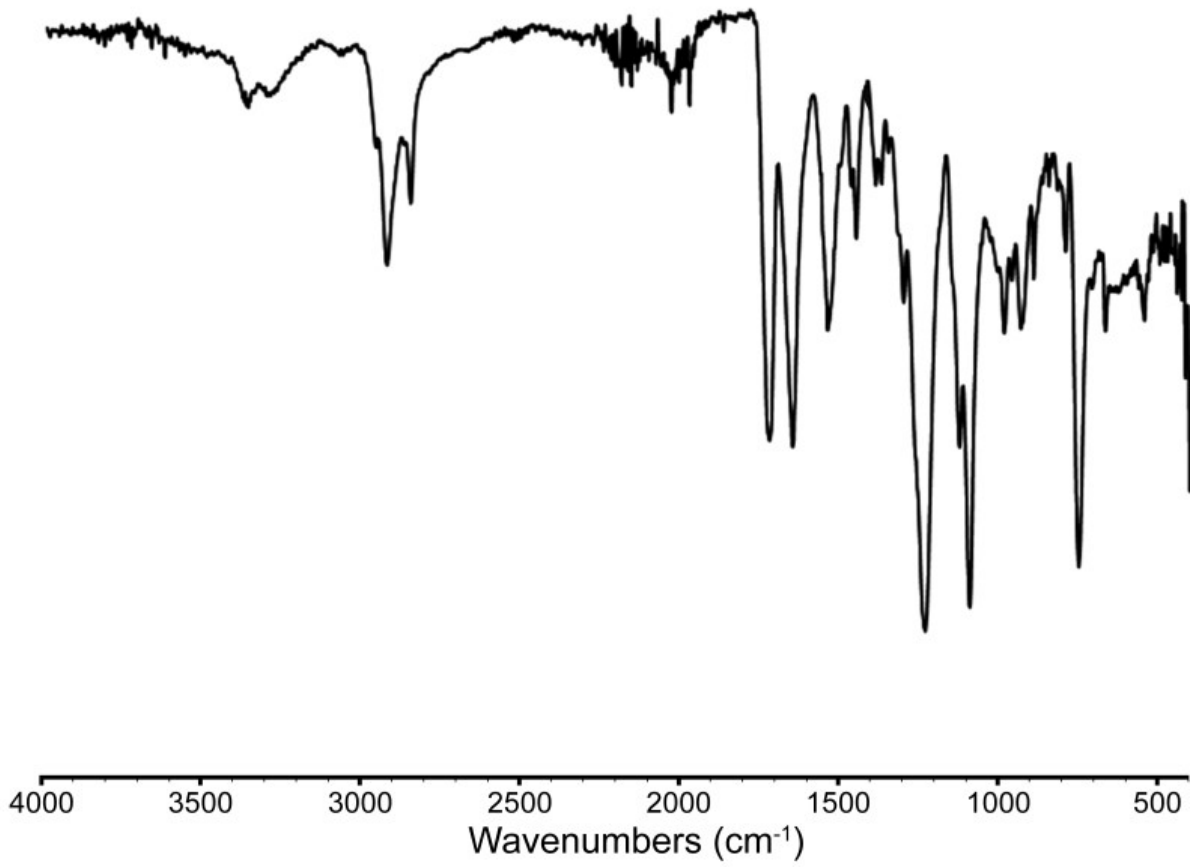

Fig. S45. FT-IR spectrum of **P14**.

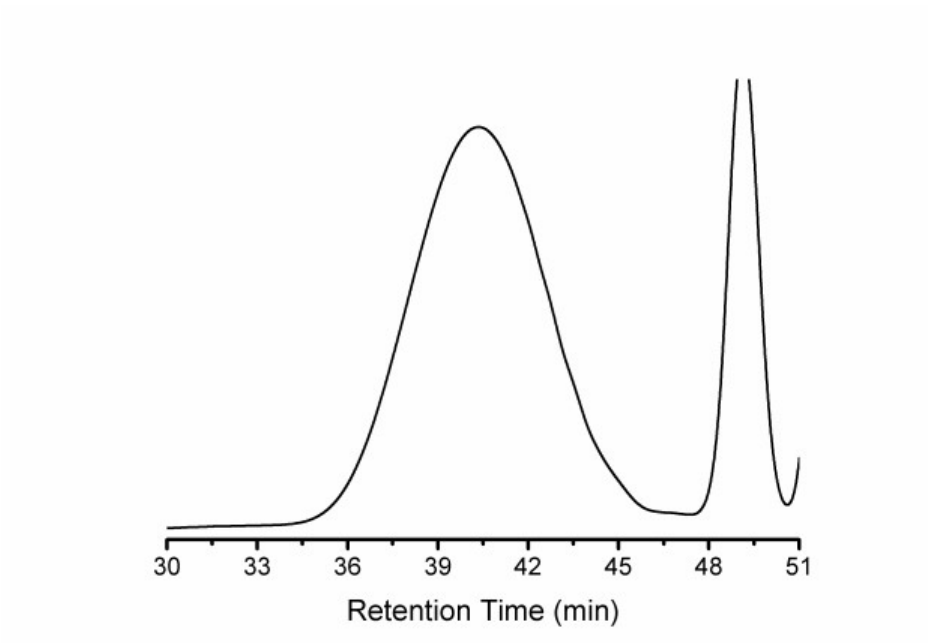

Fig. S46. GPC trace of **P14**.

Synthesis of P15

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), 1,4-butanediol (82.6 mg, 0.920 mmol, 1 equiv), 2,3,4,5,6-pentafluorobenzaldehyde (539 mg, 2.75 mmol, 3 equiv) and CHI (342 µL, 2.75 mmol, 3 equiv) were used. The resulting white sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 346 mg, 41%). ^{1}H NMR ($CDCl_3$, δ) 8.15-8.01 (m, 2H, Ar*H*), 7.03-6.90 (br, 2H, N*H*), 6.64 (br, 2H, OC*H*C=O), 4.45 (br, 4H, C=OOCH_2), 3.81 (br, 2H, NHC*H*), 1.93-1.14 (m, 24H, CH_2 of cyclohexane and C=OOCH$_2$CH_2); ^{13}C NMR ($CDCl_3$, δ) 165.53, 164.02, 146.72, 144.74, 142.99, 141.06, 138.58, 136.54, 133.87, 130.73, 109.99, 66.48, 49.02, 32.57, 29.32, 25.43, 24.87.

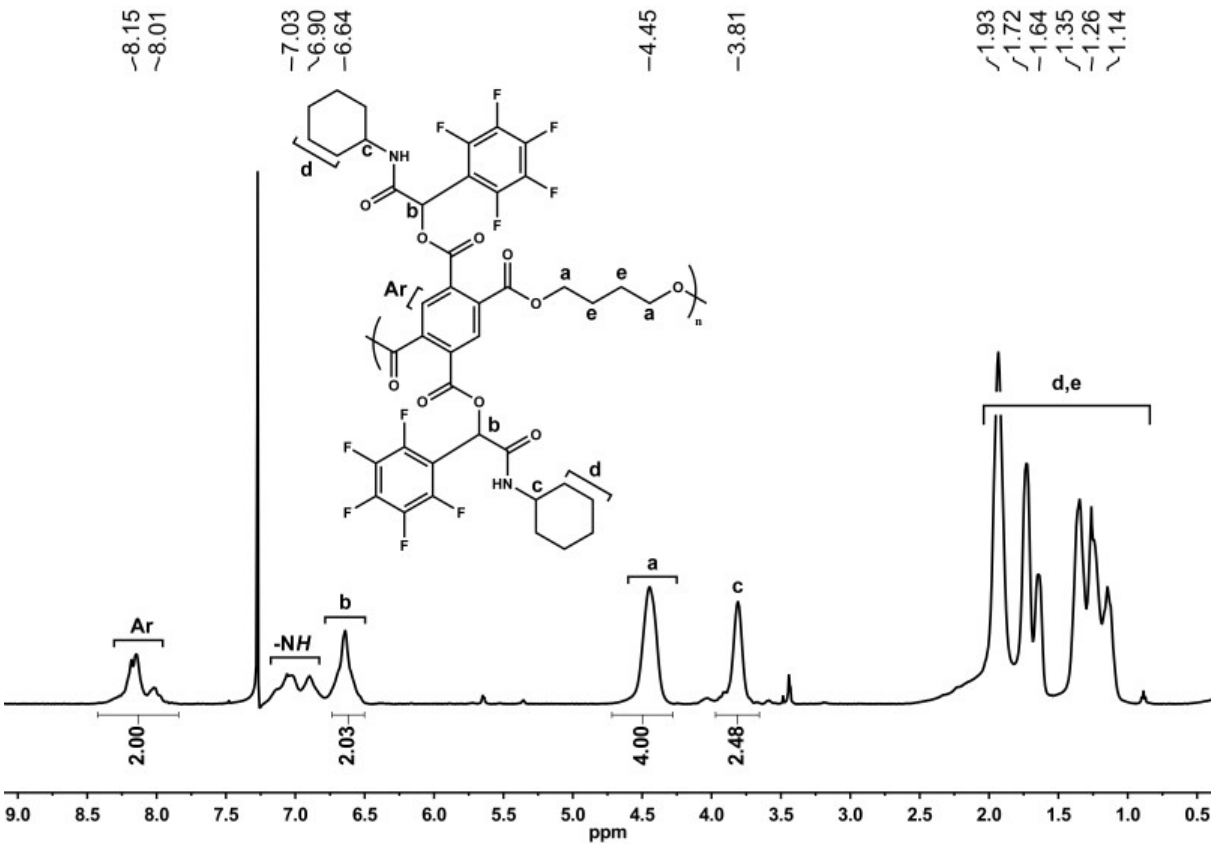

Fig. S47. ^{1}H NMR spectrum of **P15** in $CDCl_3$ (500 MHz).

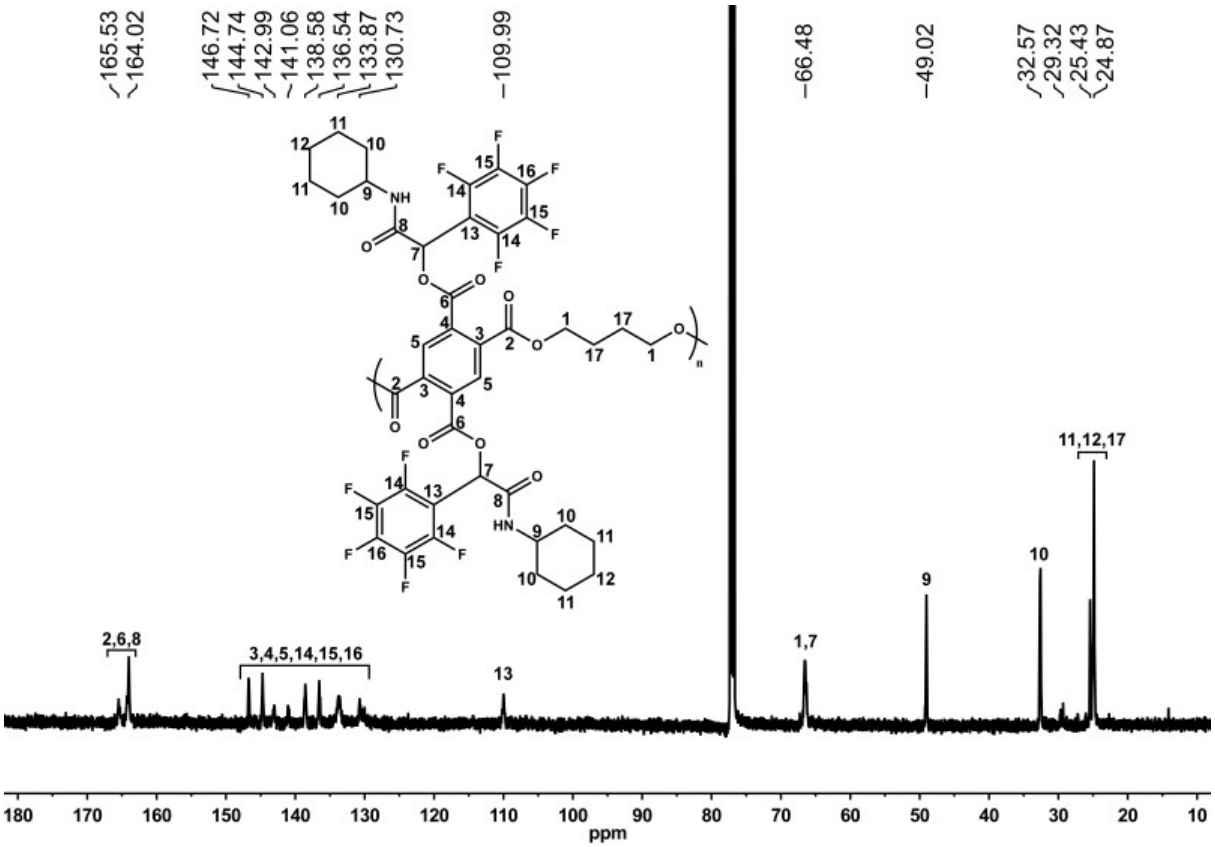

Fig. S48. ^{13}C NMR spectrum of **P15** in $CDCl_3$ (125 MHz).

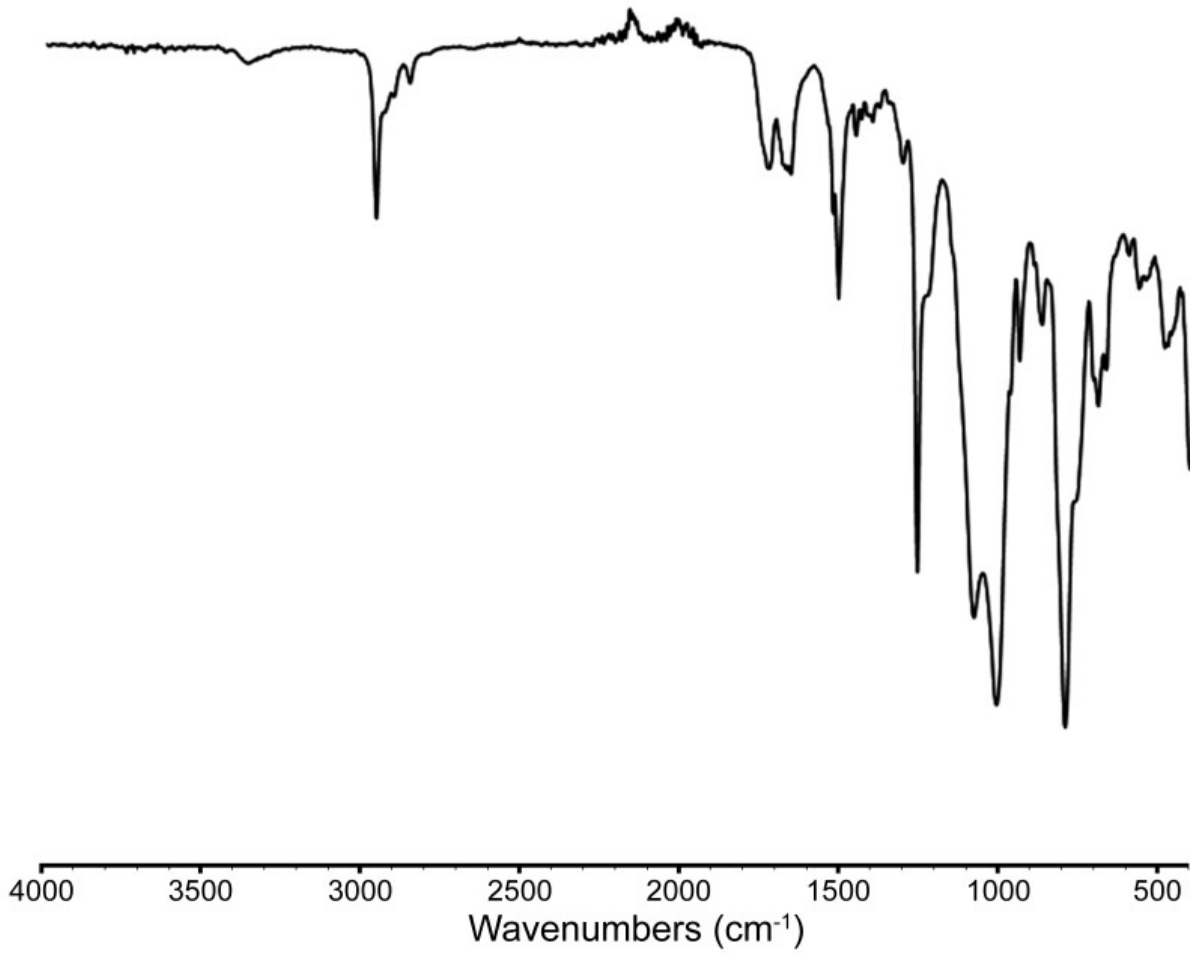

Fig. S49. FT-IR spectrum of **P15**.

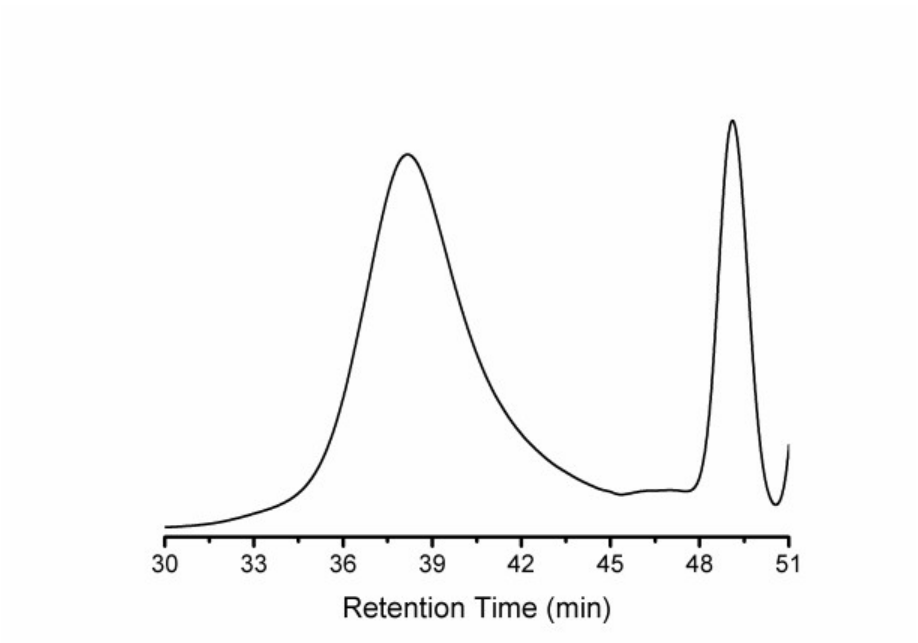

Fig. S50. GPC trace of **P15**.

Synthesis of P16

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), 1,4-butanediol (82.6 mg, 0.920 mmol, 1 equiv), cyclohexanecarboxaldehyde (333 µL, 2.75 mmol, 3 equiv) and CHI (342 µL, 2.75 mmol, 3 equiv) were used. The resulting white sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 100 mg, 14%). ^{1}H NMR ($CDCl_3$, δ) 8.17-8.15 (m, 2H, Ar*H*), 6.78-6.56 (m, 2H, N*H*), 5.18-5.15 (d, 2H, OC*H*C=O), 4.41 (b, 4H, C=OOCH_2), 3.82 (b, 2H, NHC*H*), 2.08-1.11 (m, 44H, CH_2 of cyclohexane and C=OOCH$_2$CH_2); ^{3}C NMR ($CDCl_3$, δ) 167.37, 165.90, 165.24, 134.66, 134.40, 133.71, 130.73, 129.86, 80.54, 80.16, 66.05, 48.36, 39.79, 33.10, 32.72, 29.39, 27.07, 25.99, 25.53, 24.93.

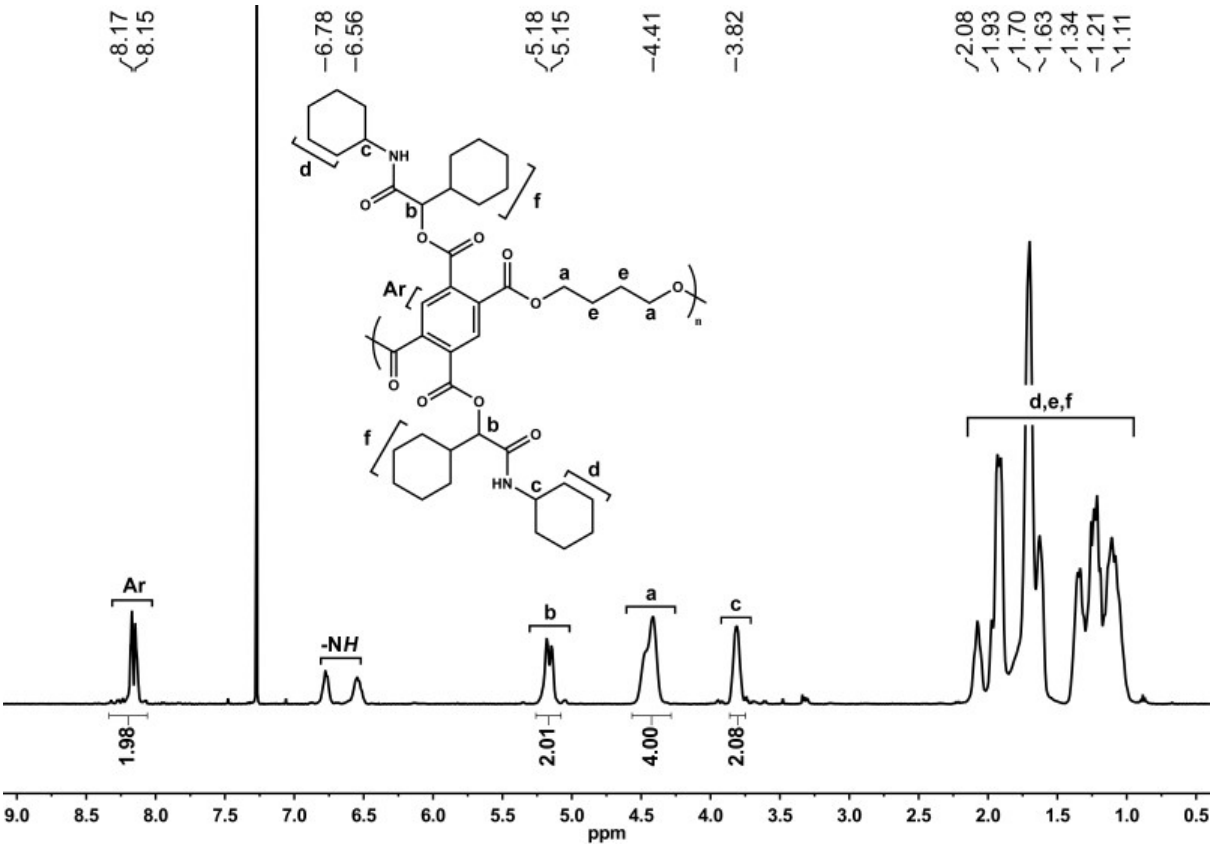

Fig. S51. ^{1}H NMR spectrum of **P16** in $CDCl_3$ (500 MHz).

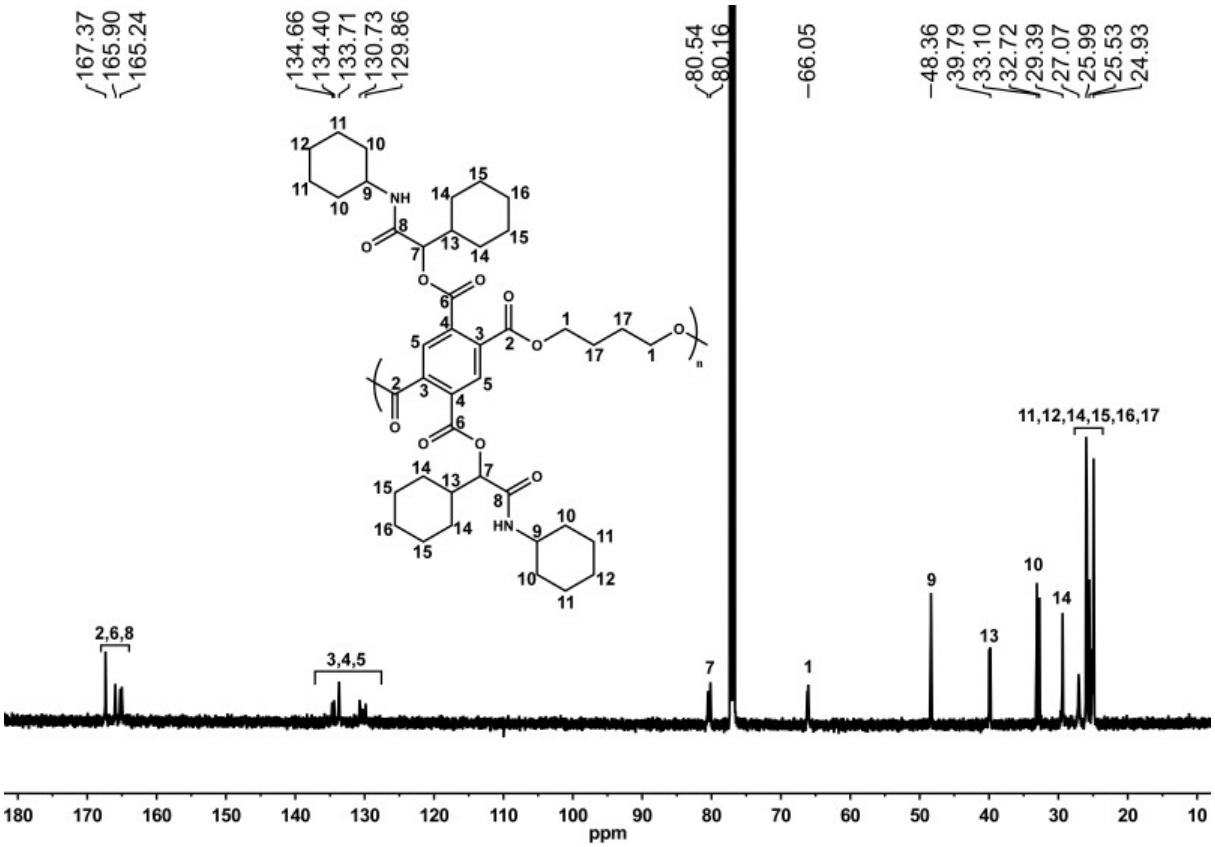

Fig. S52. ^{13}C NMR spectrum of **P16** in $CDCl_3$ (125 MHz).

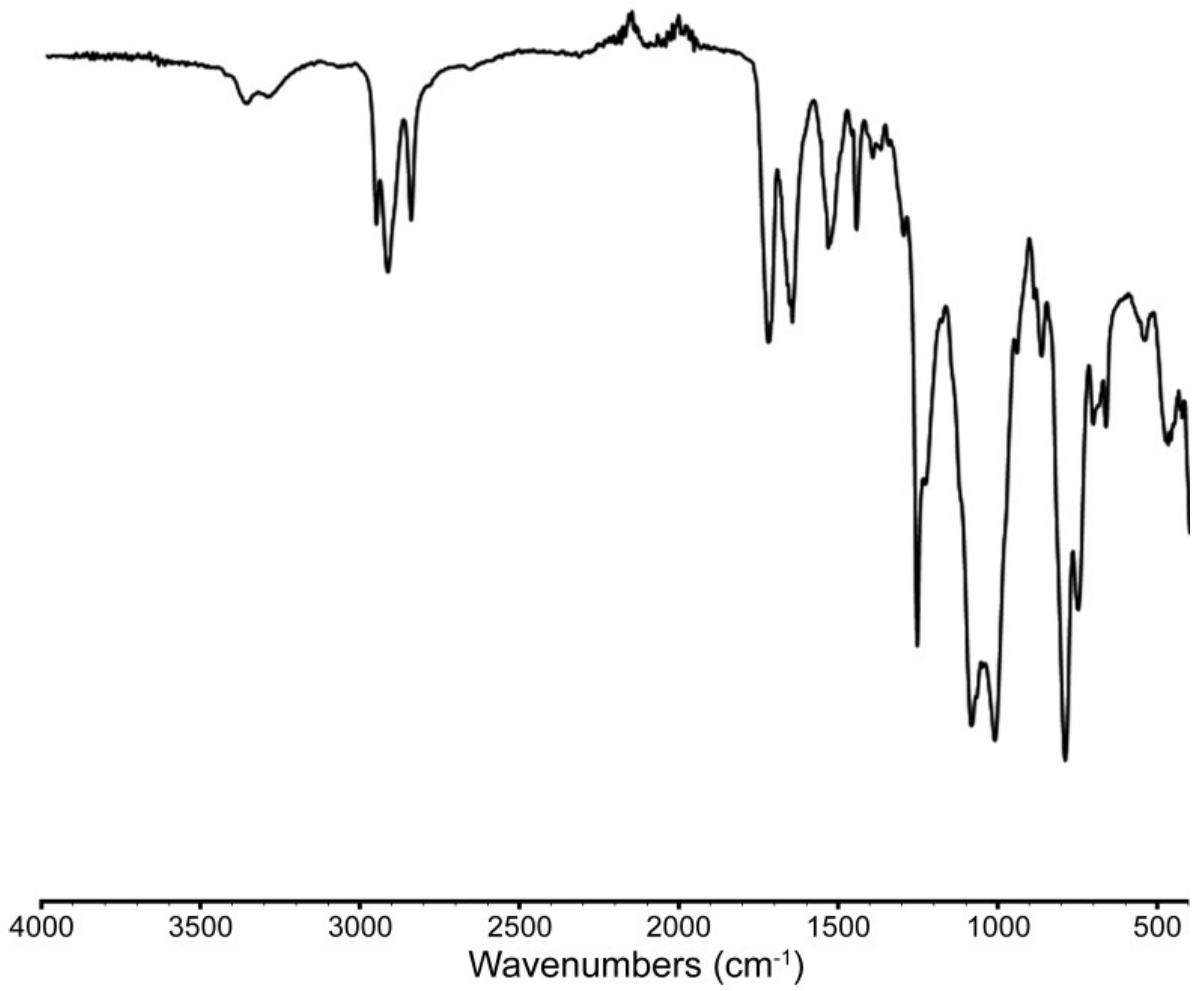

Fig. S53. FT-IR spectrum of **P16**.

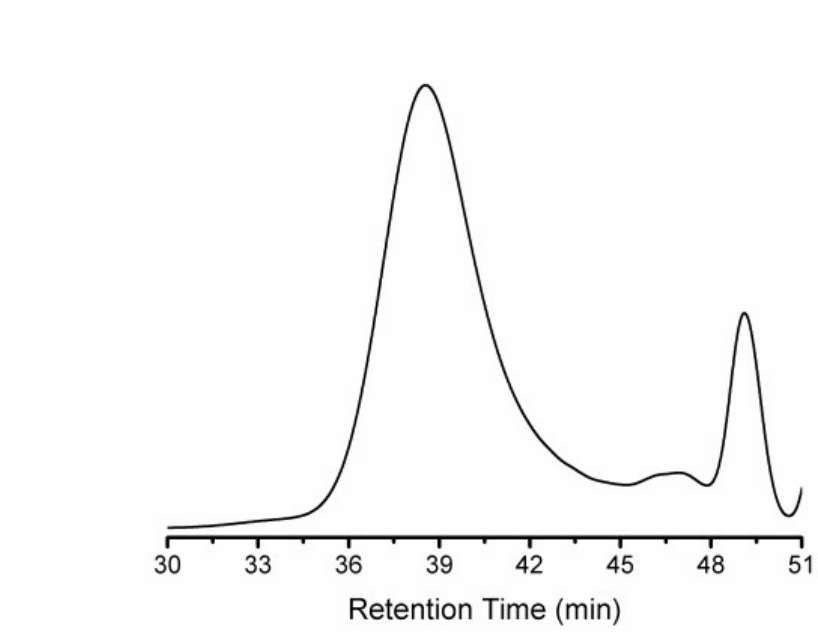

Fig. S54. GPC trace of **P16**.

Synthesis of P17

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), 1,4-butanediol (82.6 mg, 0.920 mmol, 1 equiv), 4-chlorobenzaldehyde (379 mg, 2.75 mmol, 3 equiv) and CHI (342 µL, 2.75 mmol, 3 equiv) were used. The resulting pale yellow sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 323 mg, 44%). ^{1}H NMR ($CDCl_3$, δ) 8.15-7.38 (m, 10H, Ar*H*), 6.87-6.77 (br, 2H, N*H*), 6.20 (s, 2H, OC*H*C=O), 4.32-4.20 (d, 4H, C=OOCH_2), 3.75 (m, 2H, NHC*H*), 1.85-1.14 (m, 24H, CH_2 of cyclohexane and C=OOCH$_2$CH_2); ^{3}C NMR ($CDCl_3$, δ) 166.45, 165.78, 164.67, 135.19, 133.90, 133.43, 130.47, 129.00, 76.30, 48.70, 32.75, 32.59, 25.42, 24.81.

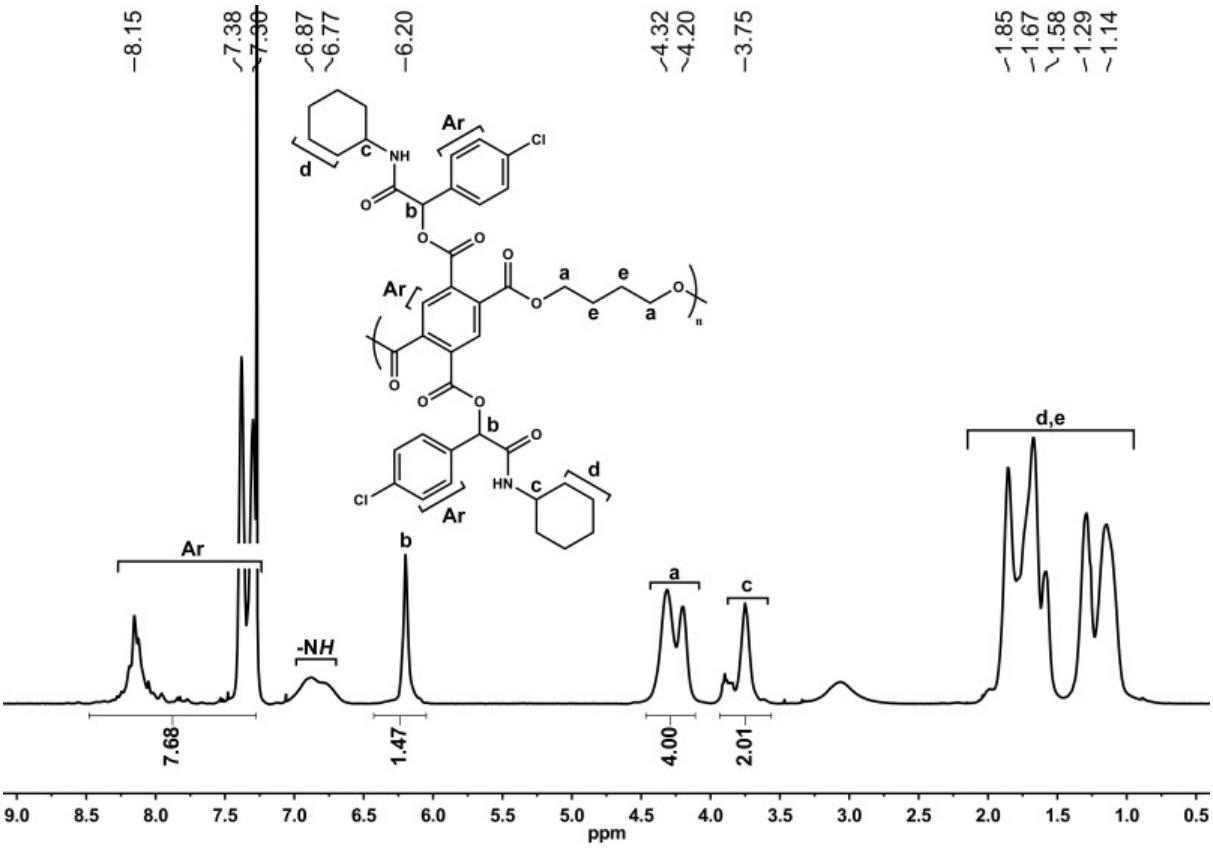

Fig. S55. ^{1}H NMR spectrum of **P17** in $CDCl_3$ (500 MHz).

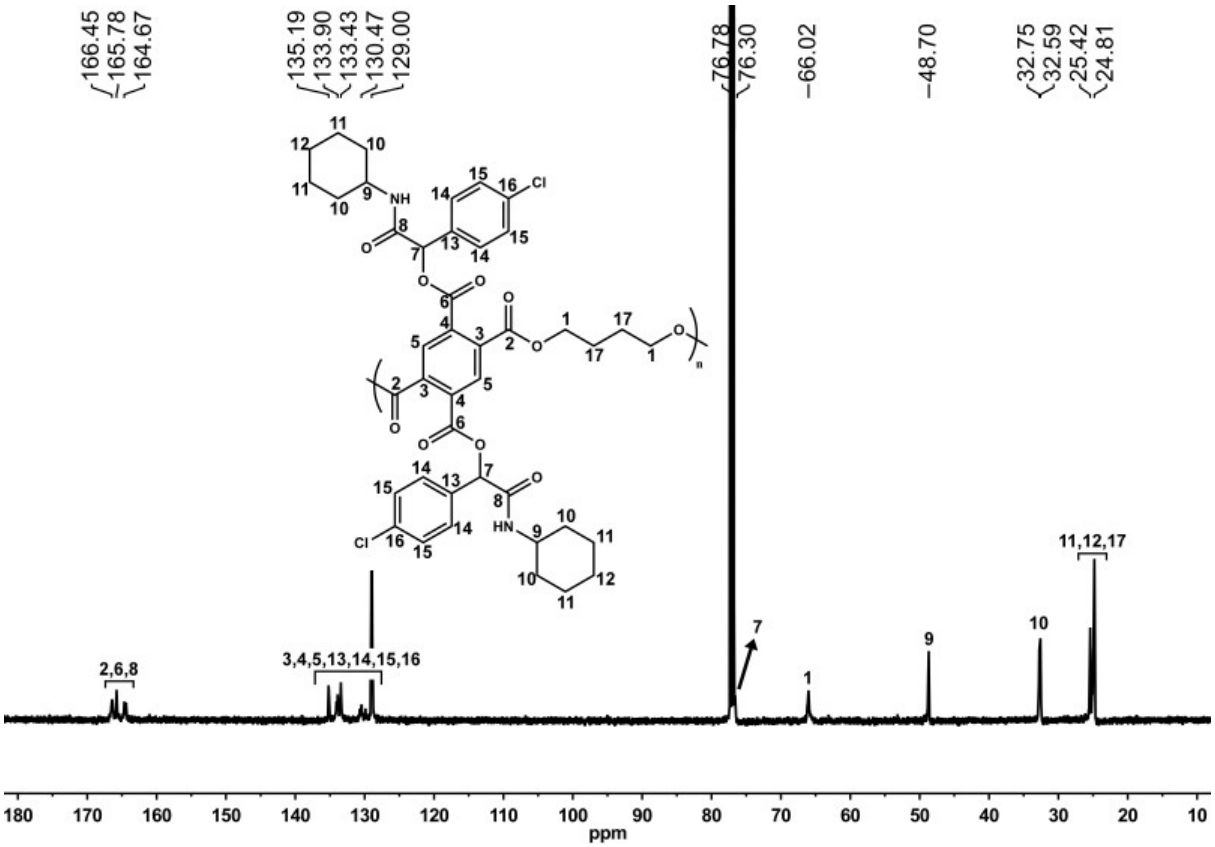

Fig. S56. ^{13}C NMR spectrum of **P17** in $CDCl_3$ (125 MHz).

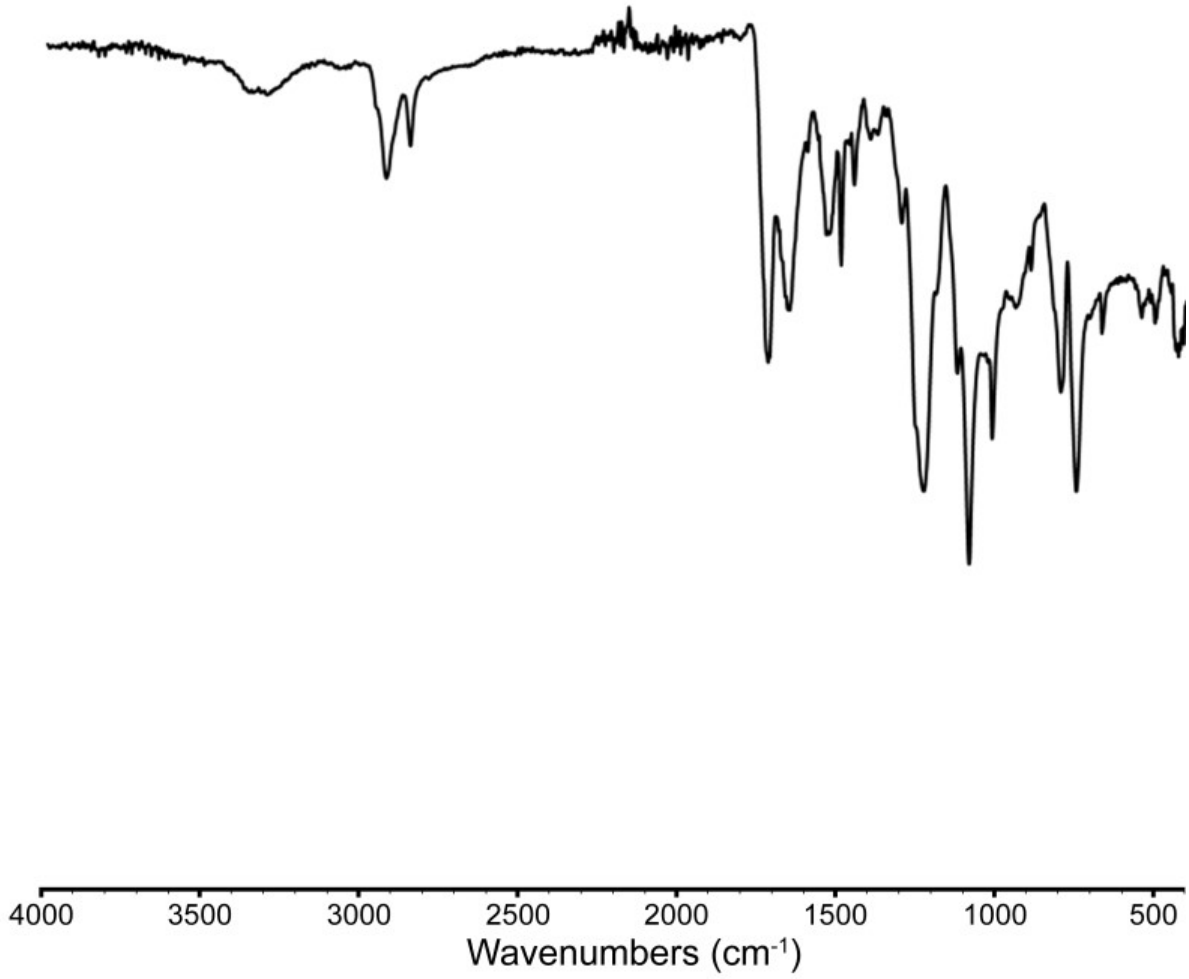

Fig. S57. FT-IR spectrum of **P17**.

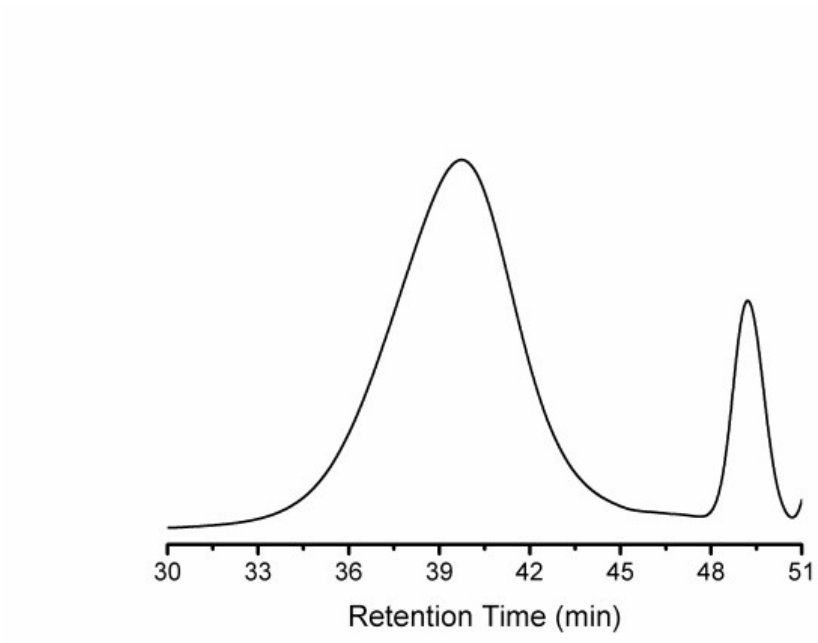

Fig. S58. GPC trace of **P17**.

Synthesis of P18

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), 1,4-butanediol (82.6 mg, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.750 mmol, 3 equiv) and benzyl isocyanide (335 µL, 2.75 mmol, 3 equiv) were used. The resulting brown sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 760 mg, 98%). ^{1}H NMR ($CDCl_3$, δ) 8.22-7.16 (m, 22H, Ar*H* and N*H*), 6.36 (br, 2H, OC*H*C=O), 4.41 (d, 4H, C=OOCH_2), 4.14 (b, 4H, ArCH_2), 1.65 (br, 4H, C=OOCH$_2$CH_2); ^{3}C NMR ($CDCl_3$, δ) 166.96, 165.30, 164.59, 148.04, 137.39, 136.67, 133.87, 130.39, 129.82, 128.58, 127.52, 123.95, 122.10, 76.09, 66.14, 62.77, 43.51, 25.61, 24.79.

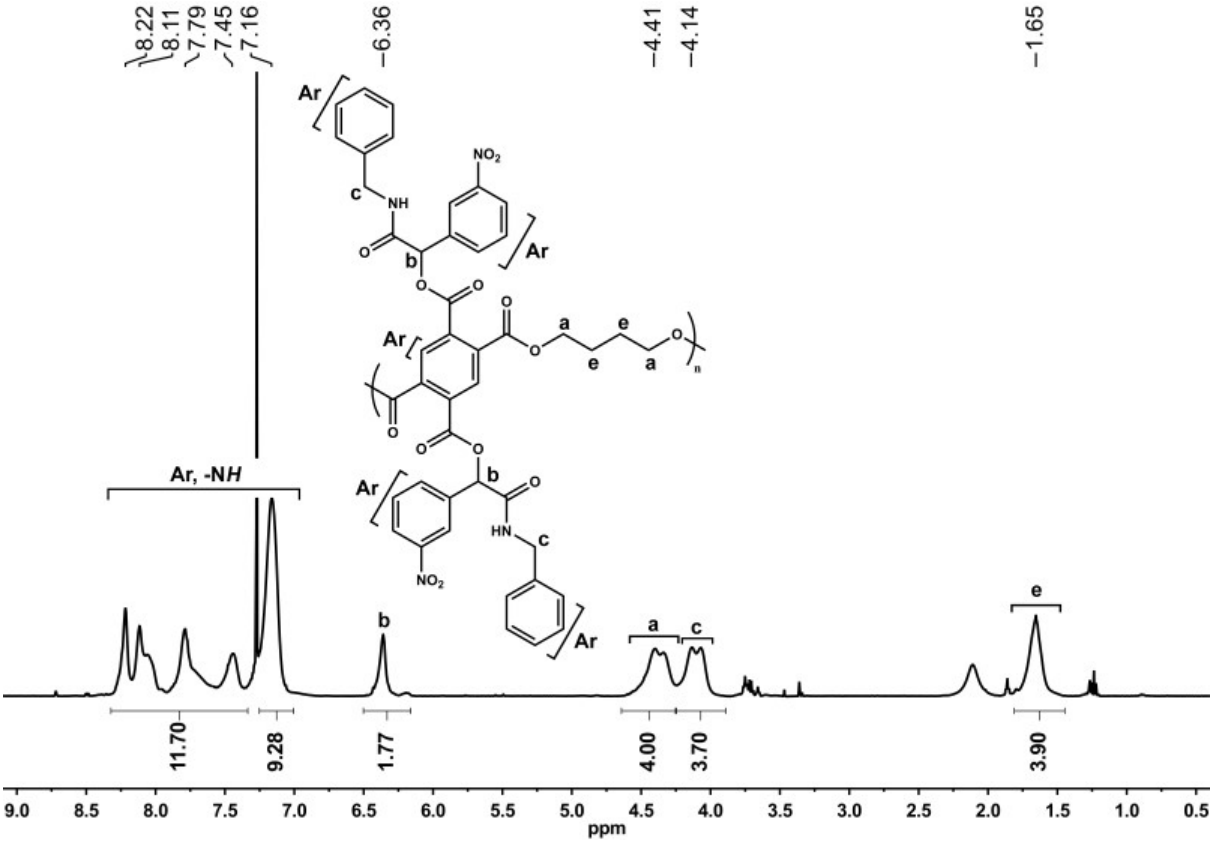

Fig. S59. ^{1}H NMR spectrum of **P18** in $CDCl_3$ (500 MHz).

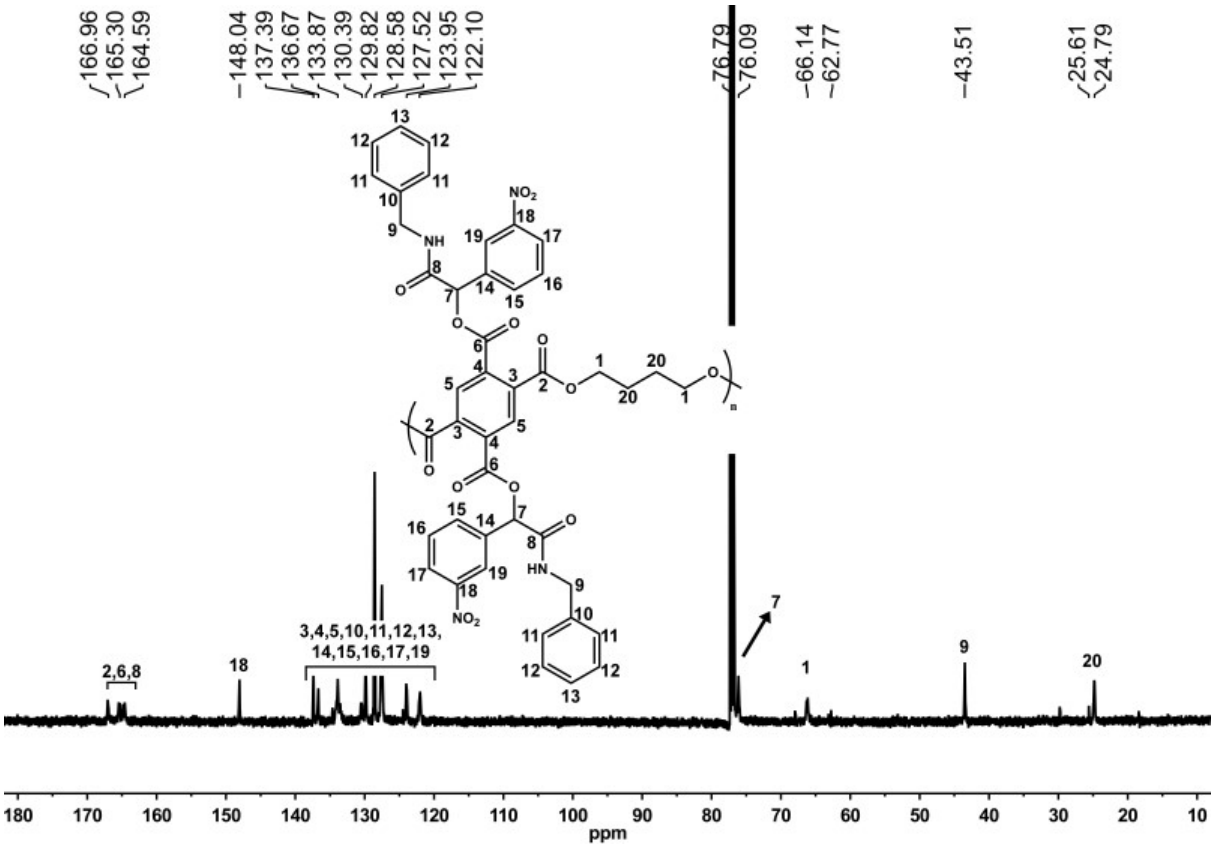

Fig. S60. ^{13}C NMR spectrum of **P18** in $CDCl_3$ (125 MHz).

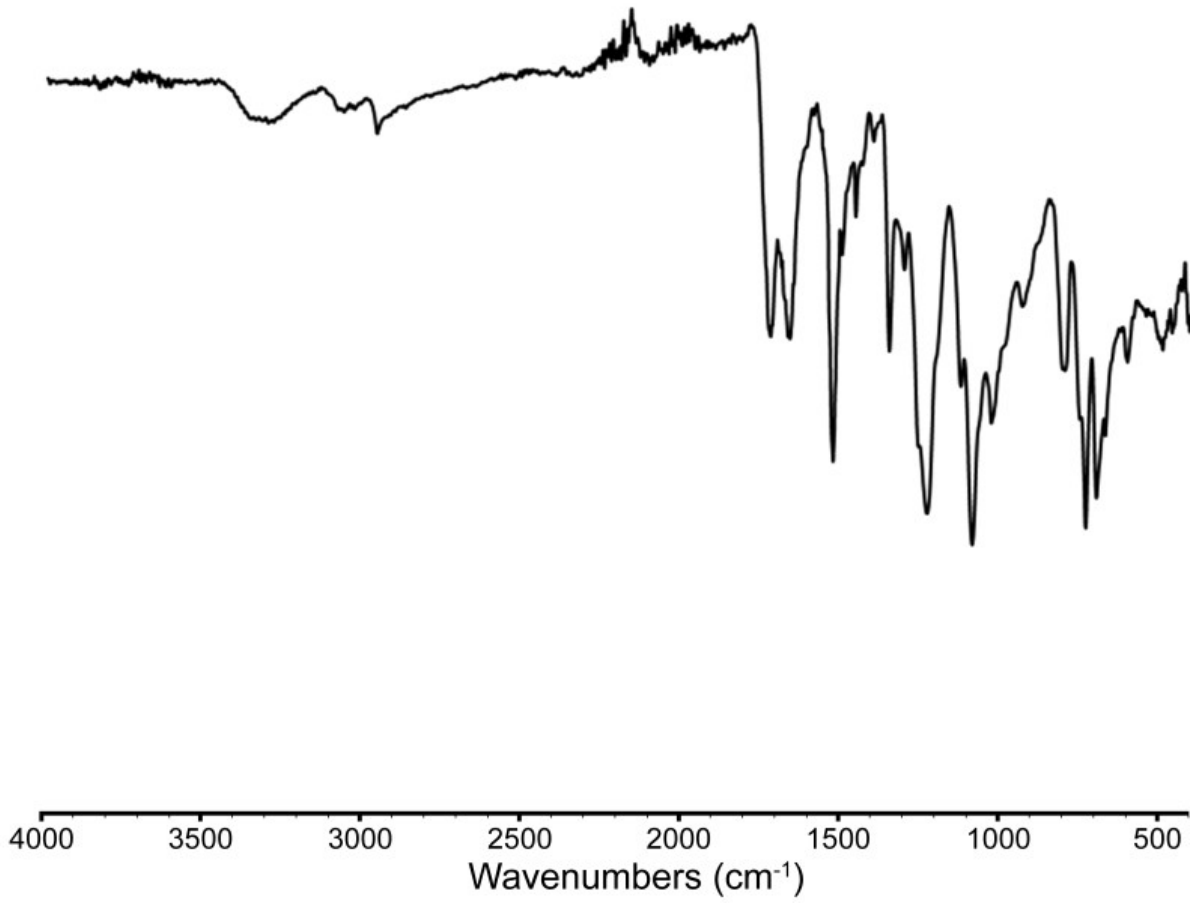

Fig. S61. FT-IR spectrum of **P18**.

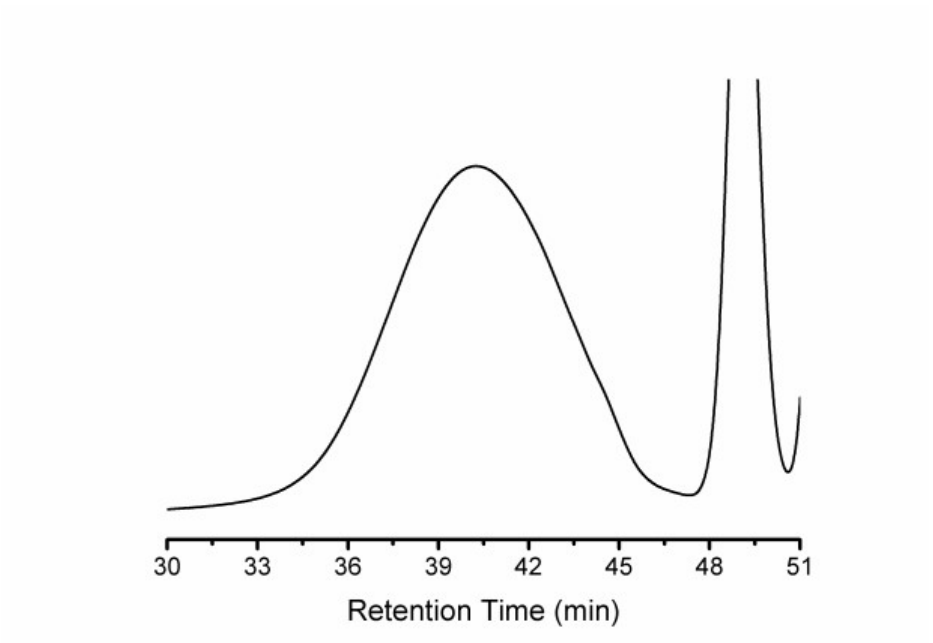

Fig. S62. GPC trace of **P18**.

Synthesis of P19

General procedure was followed. PMDA (200 mg, 0.920 mmol, 1 equiv), 1,4-butanediol (82.6 mg, 0.920 mmol, 1 equiv), m-NBA (416 mg, 2.75 mmol, 3 equiv) and *tert*-butyl isocyanide (311 µL, 2.75 mmol, 3 equiv) were employed. Solution was precipitated into 30 mL of diethyl ether and residual solvent was removed by decantation. The dissolution-precipitation process (THF-diethyl ether) was repeated two times. The resulting white solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 321 mg, 50%). ^{1}H NMR ($CDCl_3$, δ) 8.27-7.54 (m, 10H, Ar*H*), 6.99 (br, 2H, N*H*), 6.26 (br, 2H, OC*H*C=O), 4.34 (br, 4H, C=OOCH_2), 1.85 (br, 4H, C=OOCH$_2$CH_2), 1.34 (br, 18H, C(CH_3)$_3$); ^{3}C NMR ($CDCl_3$, δ) 166.09, 165.56, 164.53, 148.17, 137.08, 133.96, 129.82, 123.95, 122.06, 76.38, 66.25, 65.87, 52.17, 28.46, 24.93, 15.27.

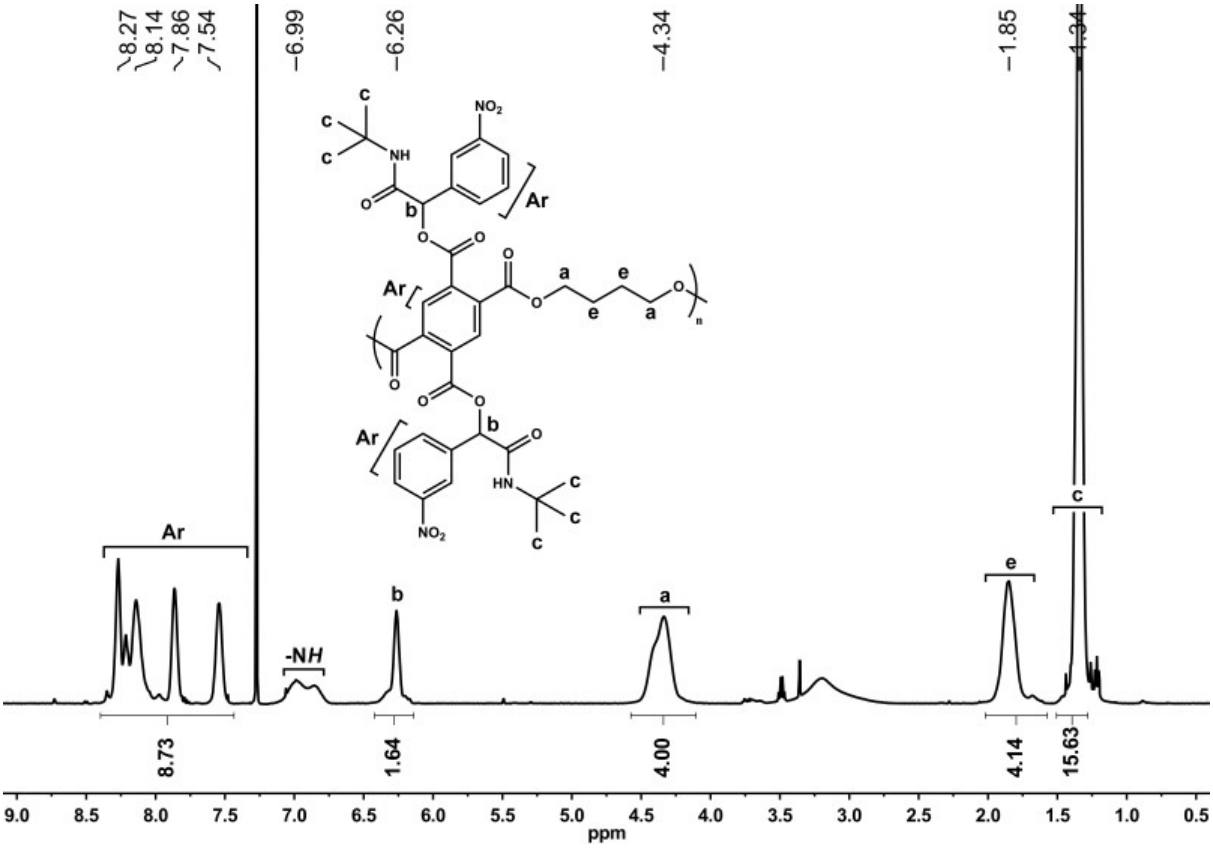

Fig. S63. ^{1}H NMR spectrum of **P19** in $CDCl_3$ (500 MHz).

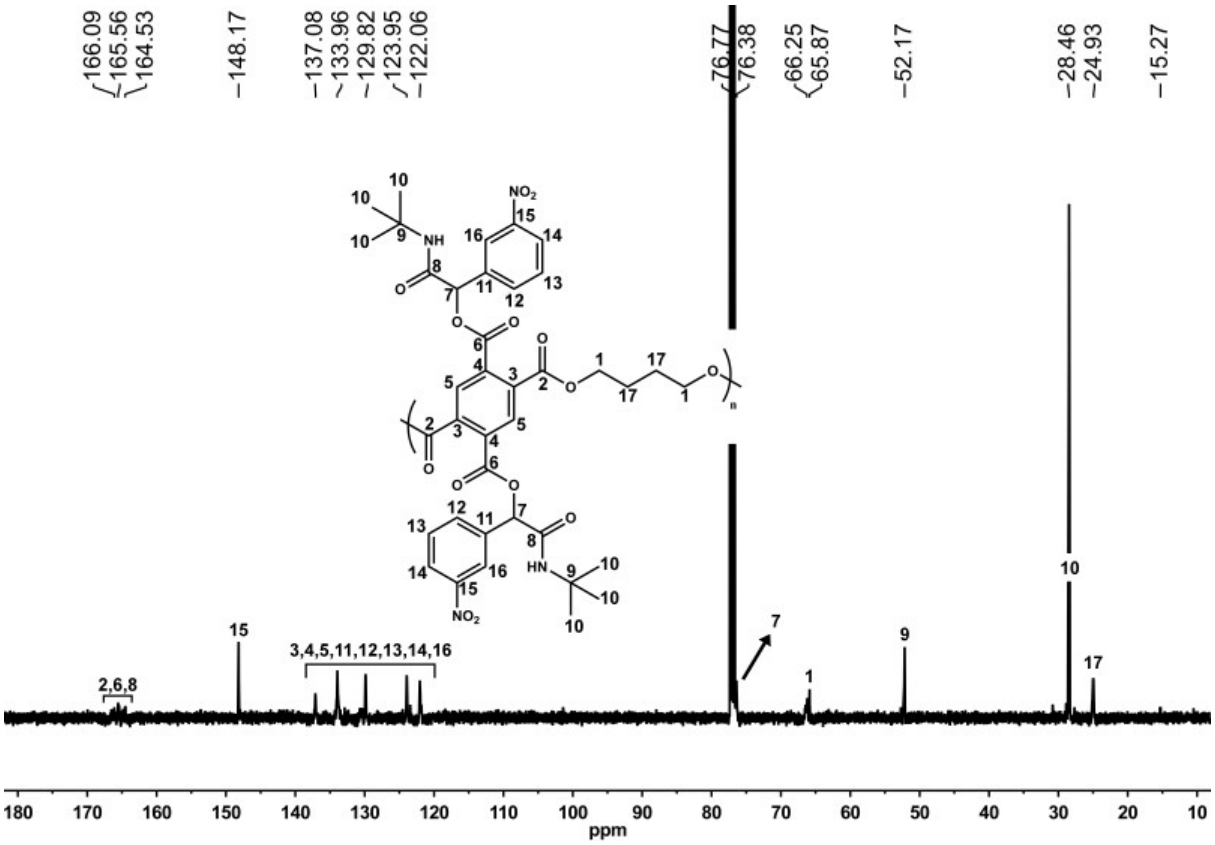

Fig. S64. ^{13}C NMR spectrum of **P19** in $CDCl_3$ (125 MHz).

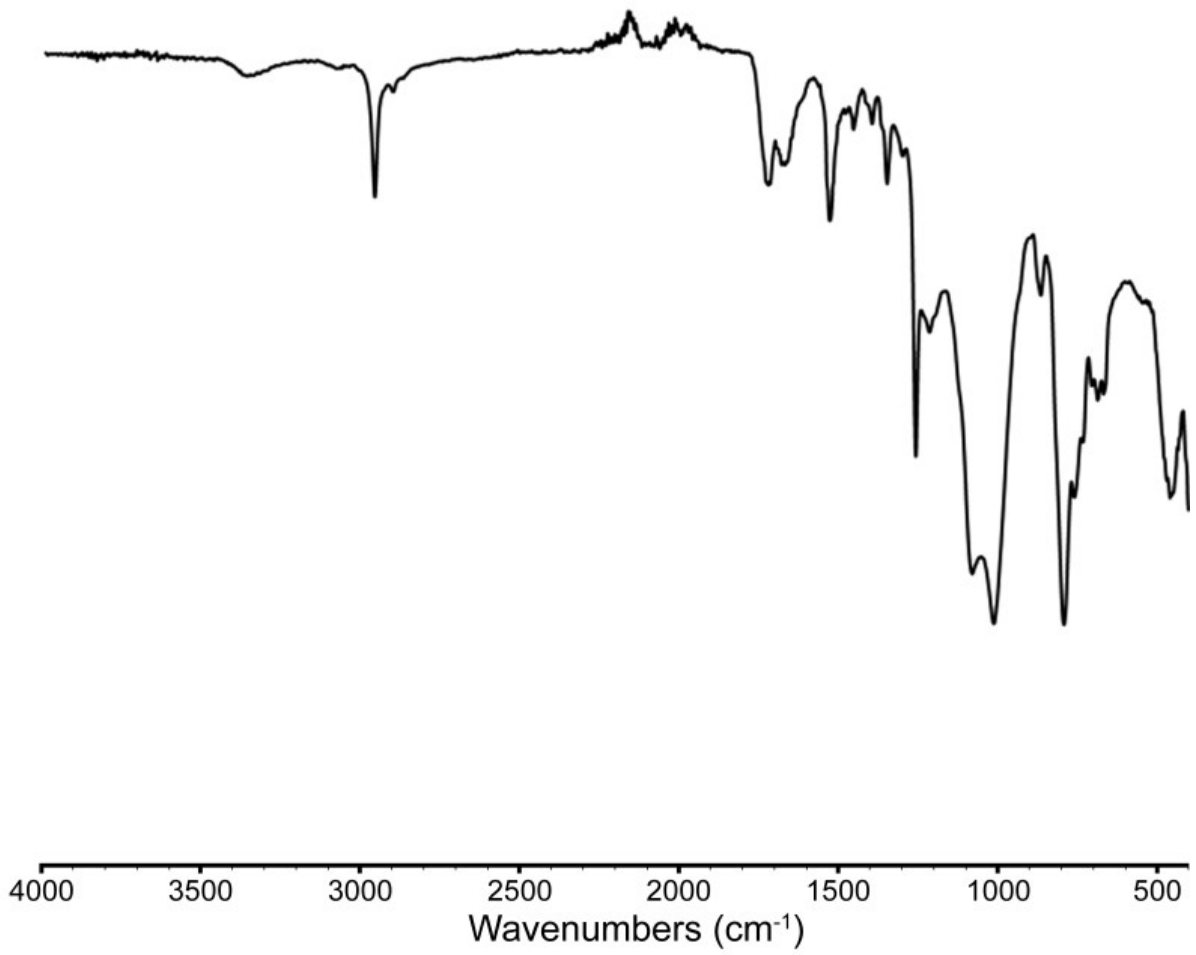

Fig. S65. FT-IR spectrum of **P19**.

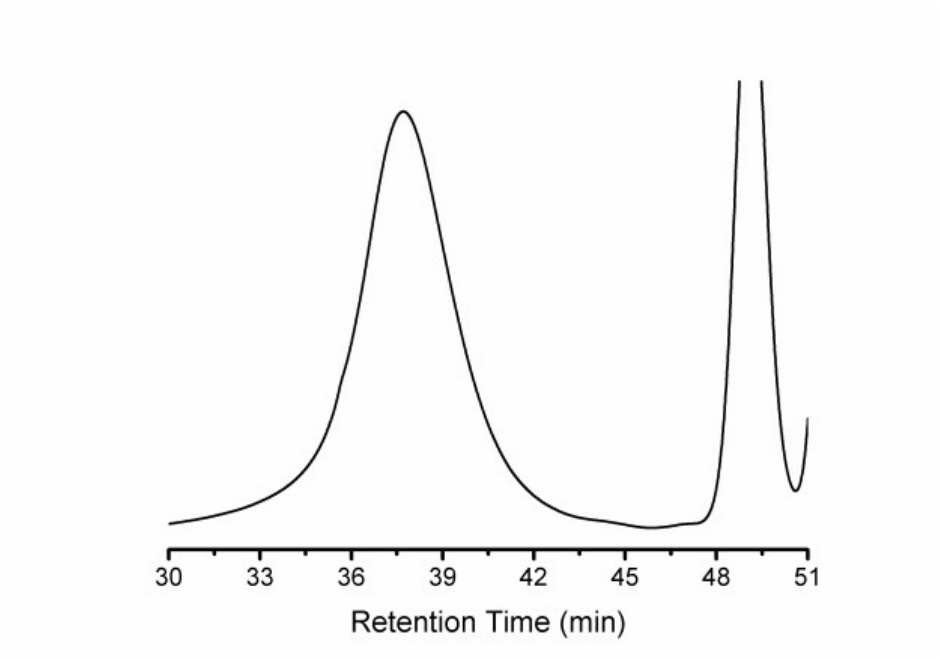

Fig. S66. GPC trace of **P19**.

Experimental Procedure for Two-step Process

Step 1:

To a 10 mL of Schlenk flask was added PMDA (200 mg, 0.920 mmol, 1 equiv) and BD (82,6 mg, 0.920 mmol, 1 equiv) which were dissolved in 2 mL of dry THF at room temperature. The reaction mixture was degassed by two FPT cycles, left in a vacuum, and stirred for 16 h at 60 ^{o}C. After the specified time, the flask was cooled to room temperature and the solution was precipitated into 30 mL of methanol, a white solid precipitated out and filtered. Afterward, the methanol solution was evaporated to give a residue which was then dissolved in 2 mL of acetone and precipitated into 30 mL of hexane and the solid product was separated by decantation. The dissolution-precipitation process (acetone-hexane) was repeated three times. The resulting white waxy solid product was left to dry in a vacuum oven for 24 h. (Yield = 252 mg, 79%) ^{1}H NMR (acetone-*d6*), δ) 8.26-7.98 (m, 2H, Ar*H*), 4.40 (m, 4H, OCH_2CH$_2$), 1.92-1.66 (m, 4H, OCH$_2$CH_2).

Step 2:

Isolated intermediate oligoester (200 mg, 0.574 mmol, 1 equiv) was added to a 10 mL of Schlenk flask and dissolved in 2 mL of dry THF and followed by the addition of m-NBA (260 mg, 1.72 mmol, 3 equiv per repeating unit) and CHI (213 μL, 1.72 mmol, 3 equiv per repeating unit), respectively. The reaction mixture was degassed by two FPT cycles and stirred at 60 ˚C for 16 h. After the specified time, the solution was precipitated into 30 mL of acidified methanol and residual solvent was removed by decantation. The dissolution-precipitation process (THF-acidified methanol) was repeated two times. The resulting white sticky solid polymer was left to dry in a vacuum oven for 24 h. (Yield = 495 mg, 91%). ^{1}H NMR (CDCl$_3$, δ) 8.27-7.27 (m, 10H, Ar*H*), 7.20-7.07 (br, 2H, N*H*), 6.33 (br, 2H, OC*H*C=O), 4.36 (br, 4H, OCH_2), 3.76 (br, 2H, NHC*H*), 1.86-1.09 (m, 24H, cyclohexyl and main chain CH_2).

Results for Two-Step Process

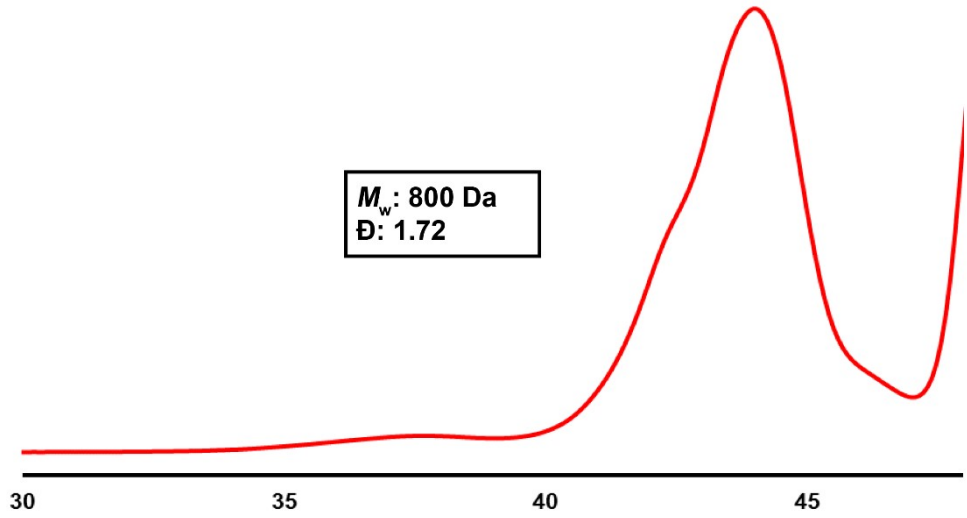

Fig. S67. GPC trace of intermediate oligoester formed in step 1 in the two-step process.

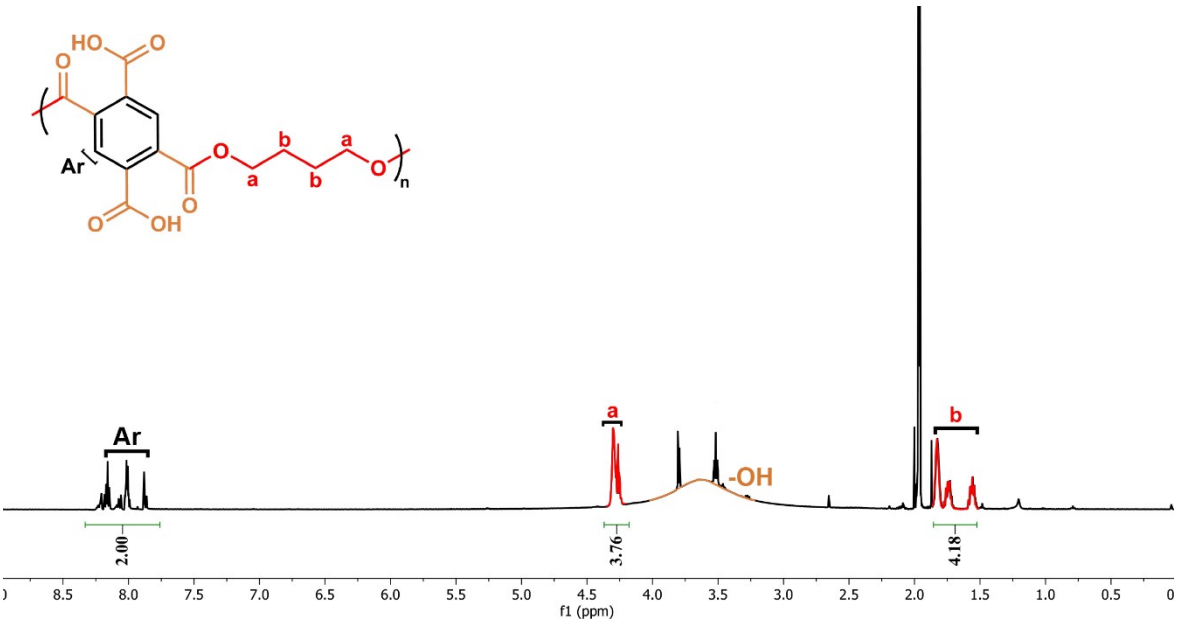

Fig. S68. ^{1}H NMR spectrum of intermediate oligoester formed in step 1 in the two-step process in acetone-*d6* (500 MHz).

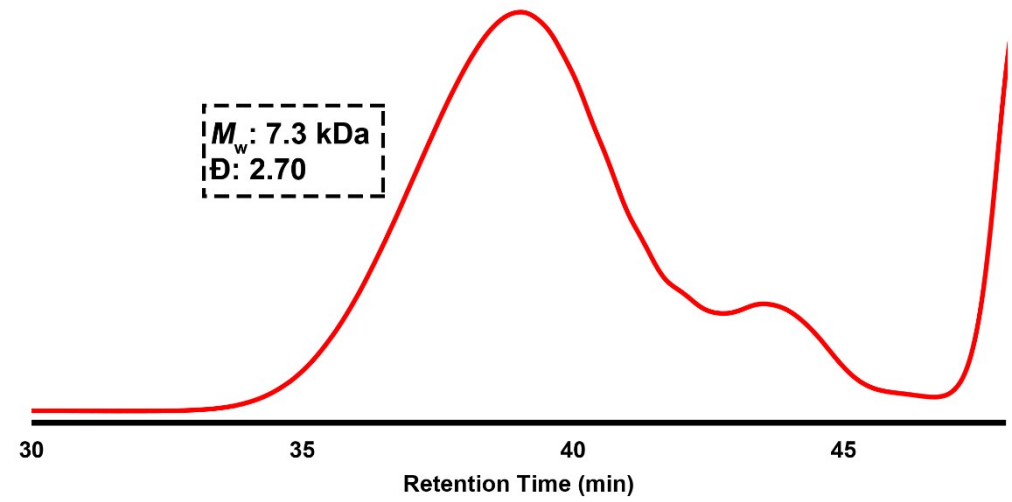

Fig. S69. GPC trace of P1 obtained from step 2 in the two-step process.

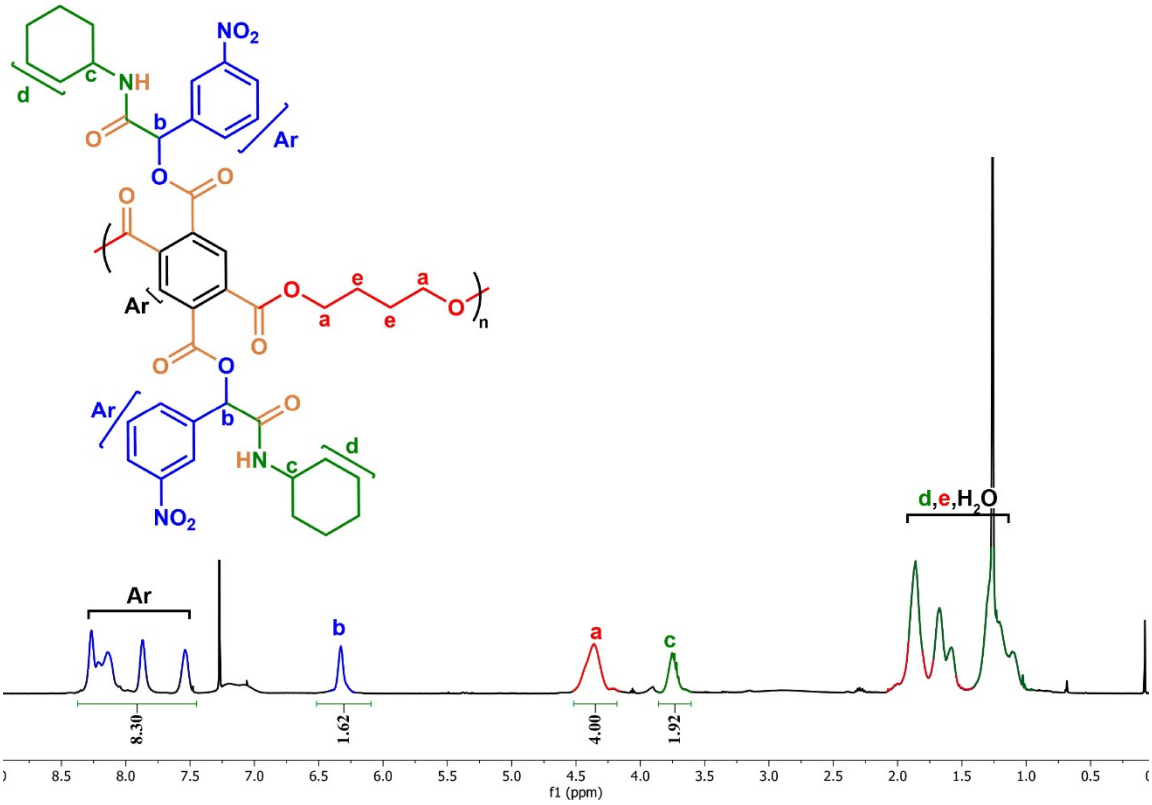

Fig. S70: ^{1}H NMR spectrum of P1 obtained from step 2 in the two-step process in $CDCl_3$ (500 MHz).