Supporting information for

Synthesis of high molecular weight poly(*p*-benzamide)s

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Synthesis of the ethyl ester monomers **M2** to **M5**.

In order to avoid the side reactions described in the first part of the report we first investigated 4-aminobenzoate monomers carrying ethyl esters. We hypothesized that ethyl esters would be less electrophilic and therefore less likely to undergo nucleophilic attack by LiHMDS or KHMDS. Moreover, different amine substituents were used in order to observe their influence on the molecular weight. Figure 5 describes the synthesis of ethyl ester monomers **M2**-**M5**. Starting from 4-amino salicylic acid the amine was first *N*-Boc protected using di-tert-butyl-di-carbonate (**7**, 91 %). Alkylation with 2-ethyl-hexyl bromide gave the ether and ester derivative **8** in 92 % yield. Hydrolysis of the ester using NaOH gave the free amino acid (**9**, 85 %) which was subsequently esterified using ethanol (**10**, 91 %). The amine substituent was introduced via substitution with allyl bromide (ethyl 2-((2-ethylhexyl)oxy)-4-((1-phenylethyl)amino)benzoate **M3**, 26%) or reductive amination with acetone (ethyl 2-((2-ethylhexyl)oxy)-4-(isopropylamino)benzoate **M2**, 58%) or acetophenone (ethyl 4-(allylamino)-2-((2-ethylhexyl)oxy)benzoate **M4**, 15%). Ethyl 4-((2-ethylhexyl)amino)benzoate **M5** was synthesized via direct reductive alkylation of 4-aminobenzoic acid with 2-ethyl hexanal (**11**, 92%) followed by esterification with ethanol (**M5**, 89%).

The solubility of the monomers **M2**-**M4** as well as of the corresponding polymers was ensured by the 2-ethylhexyl ether side chain in 2 position. Monomer **M5** showed excellent solubility due to its *N*-ethyl-hexyl side chain. In this case, no other solubilizing chain is required on the aromatic ring.

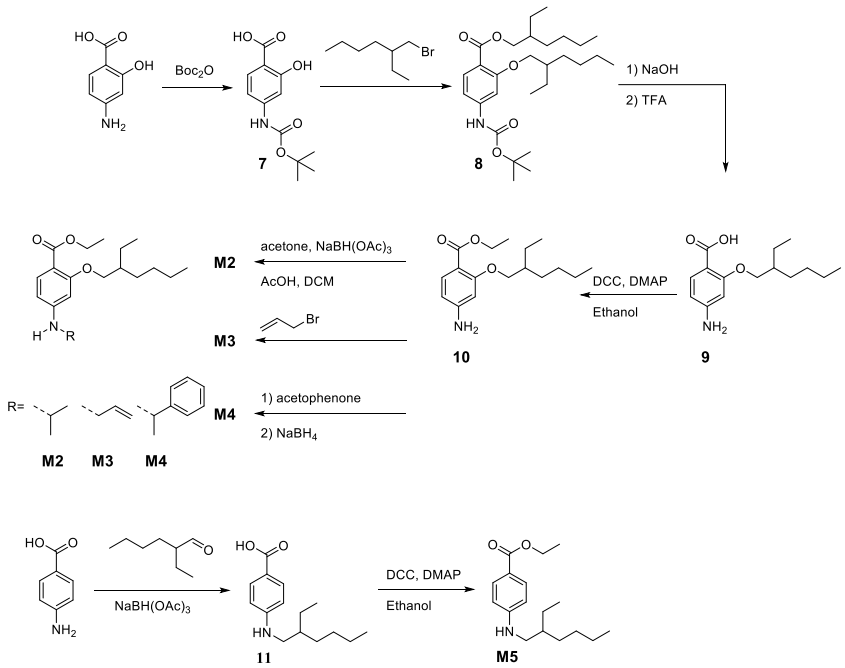


Figure S1 Synthesis of monomers **M2**-**M5**

4-((Tert-butoxycarbonyl)amino)-2-hydroxybenzoic acid (**7**)

4-Amino-2-hydroxybenzoic acid (5 g, 32.7 mmol) was dissolved in methanol (22 ml, 1.4 M) in presence of triethylamine (5.46 ml, 39.2 mmol). Boc anhydride (7.13 g, 32.7 mmol) dissolved in THF (18 ml, 1.5 M) was added to the solution. The reaction mixture was heated at 50°C for 3 days and quenched with solution of potassium hydrogen sulfate (32.7 ml, 2 M). The aqueous phase was extracted with ethyl acetate, dried and the solvent was removed under reduced pressure to give 4-((Tert-butoxycarbonyl)amino)-2-hydroxybenzoic acid **7** (7.52 g, 29.7 mmol, 91%). ^{1}H NMR (300 MHz, DMSO-*d*6) δ ppm 1.42 - 1.60 (m, 9 H) 6.93 - 7.05 (m, 1 H) 7.14 (d, *J*=1.9 Hz, 1 H) 7.66 (d, *J*=8.7 Hz, 1 H) 9.71 (s, 1 H) 11.30 (br, 1 H). ^{13}C NMR (75 MHz, DMSO-*d*6) δ ppm 28.01 (3 Cp) 79.83 (1 Cq) 104.57 (1 Ct) 106.52 (1 Cq) 109.24 (1 Ct) 130.93 (1 Ct) 146.26 (1 Cq) 152.39 (1 Cq) 162.22 (1 Cq) 171.74 (1 Cq). [1]

2-Ethylhexyl 4-((tert-butoxycarbonyl)amino)-2-((2-ethylhexyl) oxy)benzoate (**8**)

4-((Tert-butoxycarbonyl)amino)-2-hydroxybenzoic acid **7** (7.52 g, 29.7 mmol) was dissolved with dry potassium carbonate (20.52 g, 148 mmol) in DMF (150 ml, 0.2 M) in presence of dry ether-18-crown-6 and potassium iodide. 2-Ethylhexylbromide

[1] Dhaneshwar, S. S.; Chail, M.; Patil, M.; Naqvi, S.; Vadnerkar, G. Colon-specific mutual amide prodrugs of 4-aminosalicylic acid for their mitigating effect on experimental colitis in rats. *Eur. J. Med. Chem.*, **2009**, *44*, 131-142.

(12.74 ml, 71.3 mmol) was added to the solution under a gentle flow of argon. The solution was then heated at reflux (95°C) for 72 hours. The suspension was pourred into water and left one night precipitating. Product was filtered off and redissolved in DCM. Solution was dried and the solvent removed under reduced presssure. Product was dried on a Schlenk line and purified by column chromatography using ethyl acetate/hexane (1:4) as eluent to obtain a slightly red oil **8** (13g, 27.2 mmol, 92%). ^{1}H NMR (360 MHz, CHLOROFORM-*d*) δ ppm 0.75 - 1.00 (m, 12 H) 1.02 - 1.58 (m, 25 H) 1.67 (dd, *J*=10.9, 5.4 Hz, 2 H) 3.43 - 4.34 (m, 4 H) 6.84 (d, *J*=8.6 Hz, 1 H) 7.40 (br. s., 1 H) 7.73 (d, *J*=8.4 Hz, 1 H) 7.84 (br. s., 1 H). ^{13}C NMR (91 MHz, CHLOROFORM-*d*) δ ppm 10.19 - 11.13 (2 Cp) 13.74 (2 Cp) 21.81 - 24.34 (4 Cs) 27.96 (3 Cp) 28.38 - 29.14 (2 Cs) 29.71 - 30.60 (2 Cs) 38.30 - 39.57 (2 Ct) 64.72 (1 Cs) 66.61 (1 Cs) 67.57 (1 Cs) 70.60 (1 Cs) 80.18 (1 Cq) 102.01 (1 Ct) 108.88 (1 Ct) 113.62 (1 Cq) 132.56 (1 Ct) 143.90 (1 Cq) 152.45 (1 Cq) 160.25 (1 Cq) 165.99 (1 Cq).

2-(2-Ethylhexyloxy)-4-amino benzoic acid (**9**)

2-Ethylhexyl 4-((tert-butoxycarbonyl)amino)-2-((2-ethylhexyl) oxy)benzoate **8** (13 g, 27.2 mmol) was dissolved in a methanol/water (1:1, 50 ml, 0.5 M) mixture in presence of sodium hydroxyde (4.3 g, 108.8 mmol) and heated at reflux during five hours. Concentrated hydrochloric acid (37%) was added to the solution. The pH of the solution was adjusted to around 7 using sodium bicarbonate. Product was then extracted with DCM. The solution was dried and the solvent removed. The resulting yellowish oil was dissolved in a DCM trifluoroacetic acid (1:1, 25 ml, 1 M) mixture and heated at 40°C for three hours. The solution was then washed with a saturated solution of sodium carbonate and then with brine. The organic layer was dried with magnesium sulfate, the solvent removed and the crude product purified by column chromatography using ethyl acetate/hexane (1:3) as eluent to obtain 2-(2-ethylhexyloxy)-4-amino benzoic acid **9** as a yellow solid (6.13 g, 23 mmol, 85 %). ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.80 - 1.05 (m, 6 H) 1.29 - 1.59 (m, 8 H) 1.71 - 1.90 (m, 1 H) 4.06 (d, *J*=5.4 Hz, 2 H) 6.27 (d, *J*=2.1 Hz, 1 H) 6.37 (dd, *J*=8.6, 2.1 Hz, 1 H) 7.95 (d, *J*=8.6 Hz, 1 H) 9.08 - 12.41 (m, 1 H). ^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ ppm 10.03 (1 Cp) 13.28 (1 Cp) 22.83 (1 Cs) 23.88 (1 Cs) 28.88 (1 Cs) 30.46 (1 Cs) 38.41 (1 Ct) 72.06 (1 Cs) 95.90 (1 Ct) 107.09 (1 Cq) 107.82 (1 Ct) 134.72 (1 Ct) 152.76 (1 Cq) 159.58 (1 Cq) 165.81 (1 Cq).

Ethyl 4-amino-2-((2-ethylhexyl)oxy)benzoate (**10**)

2-(2-Ethylhexyloxy)-4-amino benzoic acid **9** (2.5 g, 9.42 mmol) was dissolved in DCM (18.84 ml, 0.5 M) in presence of DMAP (0.23 g, 1.884 mmol) and ethanol (5.5 ml, 94 mmol) and cooled to 0°C. DCC (2 g, 9.69 mmol) was added and the solution was stirred 5 minutes. Solution was allowed to warm to room temperature and stirred overnight. The precipitate was filtered off and the solvent removed. The product was purified by column chromatography using ethyl acetate/hexane (3:1) as eluent to obtain the product **10** as a orange liquid (2.51 g, 8.55 mmol, 91%). ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.76 - 1.04 (m, 6 H) 1.21 - 1.67 (m, 11 H) 1.67 - 1.85 (m, 1 H) 3.76 - 3.87 (m, 2 H) 3.88 - 4.07 (m, 1 H) 4.29 (q, *J*=7.1 Hz, 2 H) 6.09 - 6.30 (m, 2 H) 7.73 (d, 1 H). ^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ ppm 10.99 (1 Cp) 13.82 (1 Cp) 14.40 (1 Cp) 22.43 (1 Cs) 23.22 (1 Cs) 28.37 (1 Cs) 29.53 (1 Cs) 39.39 (1 Ct) 56.56 (1 Cs) 67.40 (1 Cs) 98.47 (s1 Ct) 106.20 (1 Ct) 107.37 (1 Cq) 134.18 (1 Ct) 150.09 (1 Cq) 159.15 (1 Cq) 166.11 (1 Cq).

Ethyl 2-((2-ethylhexyl)oxy)-4-(isopropylamino)-benzoate (**M2**)

Ethyl 4-amino-2-((2-ethylhexyl)oxy)benzoate **10** (120 mg, 409 µmol) was dissolved in DCM (409 µl, 1 M) with acetone (60.1 µl, 818 µmol) and acetic acid (117 µl, 2.045 mmol). Sodium triacetoxyborohydride (173 mg, 818 µmol) was added and the solution was stirred overnight. The reaction was quenced using sodium bicarbonate solution. The organic layer was recovered and dried. The product was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent to obtain **M2** (80 mg, 238 µmol, 58%). ^{1}H NMR (400 MHz, THF) δ ppm 0.82 - 1.02 (m, 6 H) 1.18 (d, *J*=6.2 Hz, 6 H) 1.22 - 1.39 (m, 7 H) 1.39 - 1.71 (m, 5 H) 3.65 (d, *J*=7.8 Hz, 1 H) 3.84 (t, *J*=5.0 Hz, 2 H) 4.18 (q, *J*=7.2 Hz, 2 H) 5.26 (d, *J*=7.9 Hz, 1 H) 6.08 (d, *J*=2.1 Hz, 1 H) 6.11 (s, 1 H) 7.65 (d, 1 H). ^{13}C NMR (101 MHz, THF) δ ppm 11.75 (1 Cp) 14.66 (1 Cp) 15.21 (1 Cp) 23.12 (2 Cp) 23.68 (1 Cs) 24.48 (1 Cs) 29.27 (1 Cs) 30.92 (1 Cs) 40.94 (1 Ct) 44.50 (1 Ct) 58.88 (1 Cs) 69.56 (1 Cs) 97.14 (1 Ct) 104.73 (1 Ct) 107.59 (1 Cq) 134.99 (1 Ct) 152.90 (1 Cq) 161.80 (1 Cq) 166.01 (1 Cq).

Ethyl 4-(allylamino)-2-((2-ethylhexyl)oxy)benzoate (**M3**)

To a stirring solution of ethyl 4-amino-2-((2-ethylhexyl)oxy)benzoate **10** (0.1 g, 341 µmol) in THF (682 µl, 0.5 M) with DIPEA (119 µl, 682 µmol) at 0°C, allyl bromide (29 µl, 341 µmol) was added drop by drop. The reaction was stirred 4 hours at 0°C and allowed to stirr overnight at room temperature. The solution was pourred into water and filtered. The product was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent to obtain product **M3** (30 mg, 90 µmol, 26%). ^{1}H NMR (400 MHz, THF) δ ppm 0.84 - 0.99 (m, 6 H) 1.24 - 1.69 (m, 12 H) 3.75 - 3.81 (m, 2 H) 3.84 (t, *J*=4.8 Hz, 2 H) 4.18 (q, *J*=7.1 Hz, 2 H) 5.10 (dd, *J*=10.3, 1.6 Hz, 1 H) 5.24 (dd, *J*=17.2, 1.8 Hz, 1 H) 5.55 - 5.71 (m, 1 H) 5.81 - 6.01 (m, 1 H) 6.10 - 6.15 (m, 2 H) 7.64 (d, *J*=8.4 Hz, 1 H). ^{13}C NMR (101 MHz, THF) δ ppm 11.61 (1 Cp) 14.42 (1 Cp) 14.61 (1 Cp) 24.03 (1 Cs) 24.76 (1 Cs) 30.16 (1 Cs) 31.52 (1 Cs) 40.85 (1 Ct) 46.50 (1 Cs) 60.52 (1 Cs) 70.85 (1 Cs) 96.81 (1 Ct) 104.69 (1 Ct) 108.94 (1 Cq) 115.92 (1 Cs) 134.69 (1 Ct) 136.51 (1 Ct) 154.58 (1 Cq) 162.33 (1 Cq) 166.21 (1 Cq).

Ethyl 2-((2-ethylhexyl)oxy)-4-((1-phenylethyl)amino)benzoate (**M4**)

Ethyl 4-amino-2-((2-ethylhexyl)oxy)benzoate **10** (0.5 g, 1.7 mmol) was dissolved with acetophenone (0.2 ml, 1.71 µmol) in toluene (5 ml, 0.34 M) and refluxed under Dean-Stark conditions during 3 days. Solution was cooled to room temperature and the solvent was evaporated under reduced pressure. The imine was dissolved in a mixture of methanol and THF (1:1, 14 ml, 0.05 M), placed under argon athmosphere and cooled to 0°C before sodium borohydride (64 mg, 1.7 mmol) was added. Solution was warmed to room temperature and stirred overnight. Water was added and the mixture was extracted with DCM (3 x 10 ml). The organic phase was washed wiht brine and dried over magnesium sulfate. The solvent was removed under reduced pressure and the product purified by column chromatography with neutral aluminium oxide as adsorbant using DCM/hexane (3:1) as eluent to obtain product **M4** (100 mg, 0.25 mmol, 15%). ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.80 - 1.06 (m, 6 H) 1.18 - 1.69 (m, 14 H) 1.69 - 1.82 (m, 1 H) 3.70 - 4.00 (m, 2 H) 4.11 (br. s., 1 H) 4.30 (qt, *J*=7.1, 1.4 Hz, 2 H) 6.09 - 6.30 (m, 2 H) 7.25 - 7.30 (m, 1 H) 7.31 - 7.43 (m, 4 H) 7.74 (dt, *J*=8.3, 1.4 Hz, 1 H). ^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ ppm 11.03 (1 Cp) 14.04 (1 Cp) 14.57 (1 Cp) 22.97 (1 Cs) 23.64 (1 Cs) 24.58 (1 Ct) 29.03 (1 Cs) 30.32 (1 Cs) 39.31 (1 Ct) 53.23 (1 Ct) 59.77 (1 Cs) 70.49 (1 Cs) 95.93 (1 Ct) 103.98 (1 Ct) 108.28 (1 Cq) 125.65 (2 Ct) 127.06 (1 Ct) 128.69 (2 Ct) 134.17 (1 Ct) 144.34 (1 Cq) 151.79 (1 Cq) 161.29 (1 Cq) 166.55 (1 Cq).

4-((2-ethylhexyl)amino)benzoic acid (**11**)

Para-aminobenzoic acid (10 g, 72.9 mmol) was dissolved with 2-ethylhexanal (12.51 ml, 80 mmol) in a mixture of MeOH (130 ml, 0.5 M) and acetic acid (20 ml) and was cooled to 0°C. Solution was stirred 1 hour before addition of sodium triacetoxyborohydride (30.9 g, 146 mmol). The solution was stirred overnight at room temperature and quenched with a saturated solution of sodium bicarbonate (100 ml). Product was extracted with DCM, dried over magnesium sulfate and the solvent was removed under reduced pressure. The product was purified by column chromatography using ethyl acetate/hexane (1:3) as eluent to obtain **11** (16.73 g, 67.1 mmol, 92%). ^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 0.78 - 1.04 (m, 6 H) 1.19 - 1.44 (m, 9 H) 1.57 (d, *J*=6.0 Hz, 1 H) 3.09 (d, *J*=6.2 Hz, 2 H) 6.56 (d, *J*=8.8 Hz, 2 H) 7.94 (d, *J*=8.8 Hz, 2 H). ^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ ppm 10.73 (1 Cp) 12.71 (1 Cp) 22.36 (1 Cs) 23.57 (1 Cs) 27.96 (1 Cs) 30.04 (1 Cs) 38.88 (1 Ct) 44.64 (1 Cs) 111.15 (1 Ct) 114.87 (1 Cq) 132.20 (1 Ct) 149.98 (1 Cq) 170.06 (1 Cq).

Ethyl 4-((2-ethylhexyl)amino)benzoate (**M5**)

To a stirring solution of 4-((2-ethylhexyl)amino)benzoic acid **11** (1 g, 4.02 mmol) with DMAP (98 mg, 802 µmol) and ethanol (1 ml, 17.13 mmol) in dry DCM (10 ml, 0.4 M) at 0°C, DCC (910 mg, 4.41 mmol) was added. The solution was stirred for 5 min at 0°C and then allow to stir further 3 hours at room temperature. The suspension was filtered and the solvent removed under reduced pressure. The residue was redissolved in DCM and washed with 0,5 M HCl and saturated sodium bicarbonate solution. The organic phase was dried over magnesium sulfate and the solvent was removed. The product purified by column chromatography using ethyl acetate/hexane (1:4) as eluent to obtain product **M5** as a transparent oily liquid (0.99 g, 3.57 mmol, 89%). ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.66 - 1.16 (m, 6 H) 1.18 - 1.49 (m, 11 H) 1.49 - 1.72 (m, 1 H) 3.07 (t, *J*=5.9 Hz, 2 H) 4.05 - 4.27 (m, 1 H) 4.32 (q, *J*=7.2 Hz, 2 H) 6.23 - 6.79 (dd, 2 H) 7.87 (dd, 2 H). ^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ ppm 10.45 (1 Cp) 13.63 (1 Cp) 14.04 (1 Cp) 22.69 (1 Cs) 23.86 (1 Cs) 28.29 (1 Cs) 30.27 (1 Cs) 38.59 (1 Ct) 45.47 (1 Cs) 58.99 (1 Cs) 110.80 (1 Ct) 117.00 (1 Cq) 131.06 (1 Ct) 151.53 (1 Cq) 166.42 (1 Cq).

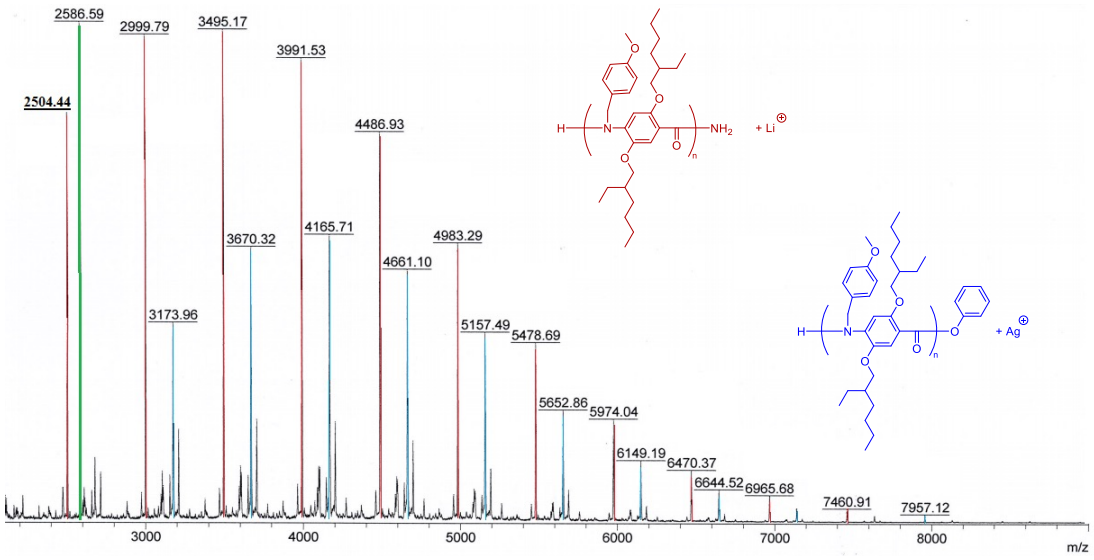


Figure S2 MALDI-TOF mass spectrum of poly(M1).

The expected distribution is shown in blue, the ester substituted distribution in red and in green a cyclic pentamer.

Side reaction studies

General procedure for the phenyl ester substitutions.

LiHMDS or KHMDS (90 µl, 1 M) was dried on a Schlenk line. Phenyl benzoate (18 mg, 90 µmol) in deuterated THF (0.75 ml, 0.12 M) was added to the base and transferred into an NMR tube. ^{1}H NMR were recorded on 400 MHz spectrometer.

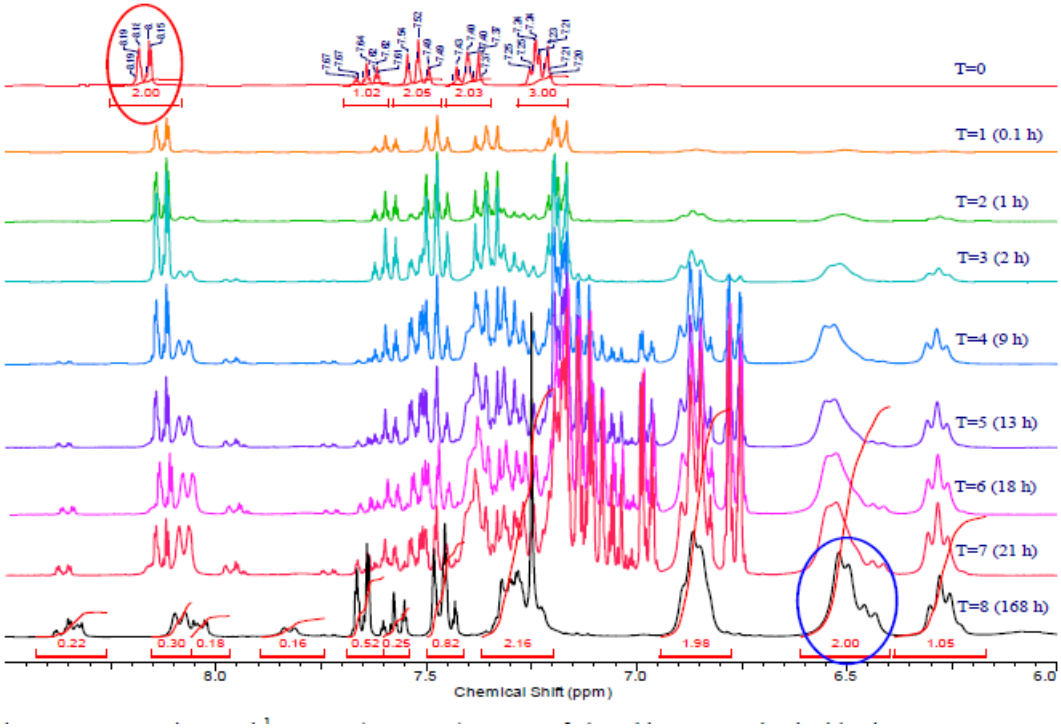


Figure S3 ^{1}H NMR spectrum (300 MHz, THF-d_8) of phenyl benzoate with LiHMDS over time.

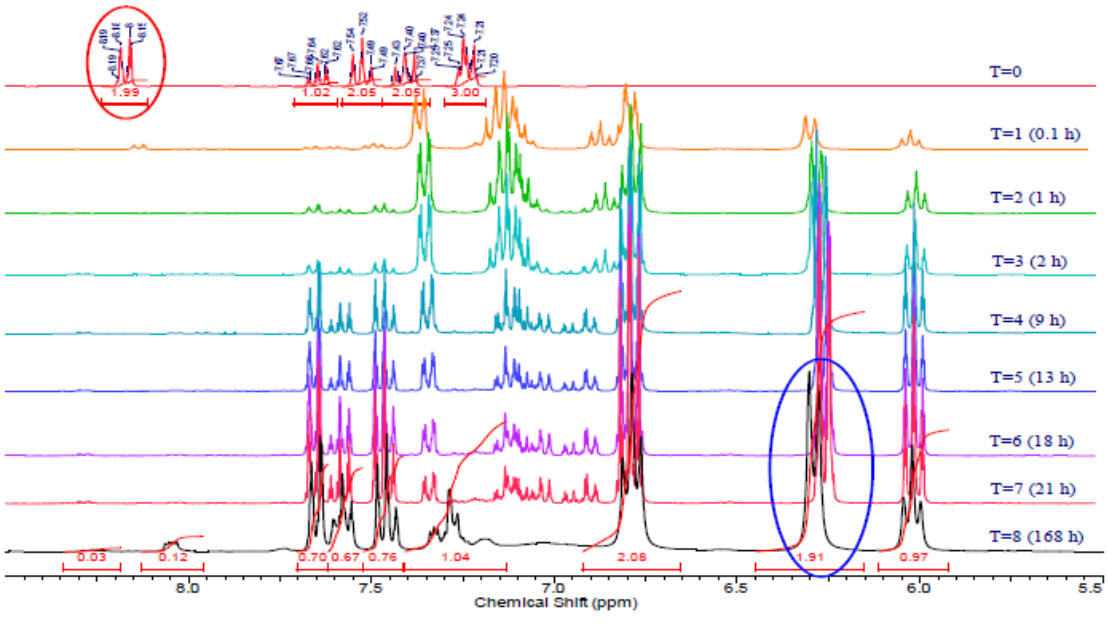


Figure S4 ^{1}H NMR spectrum (300 MHz, THF-d_8) of phenyl benzoate with KHMDS over time.

General procedure for the imine formation.

LiHMDS or KHMDS (90 µl, 1 M) was dried on a Schlenk line. *N*-benzylaniline derivatives (100 µmol) in deuterated THF (0.75 ml, 0.13 M) was added to the base and transferred into an NMR tube. 1H NMR were recorded on 400 MHz spectrometer.

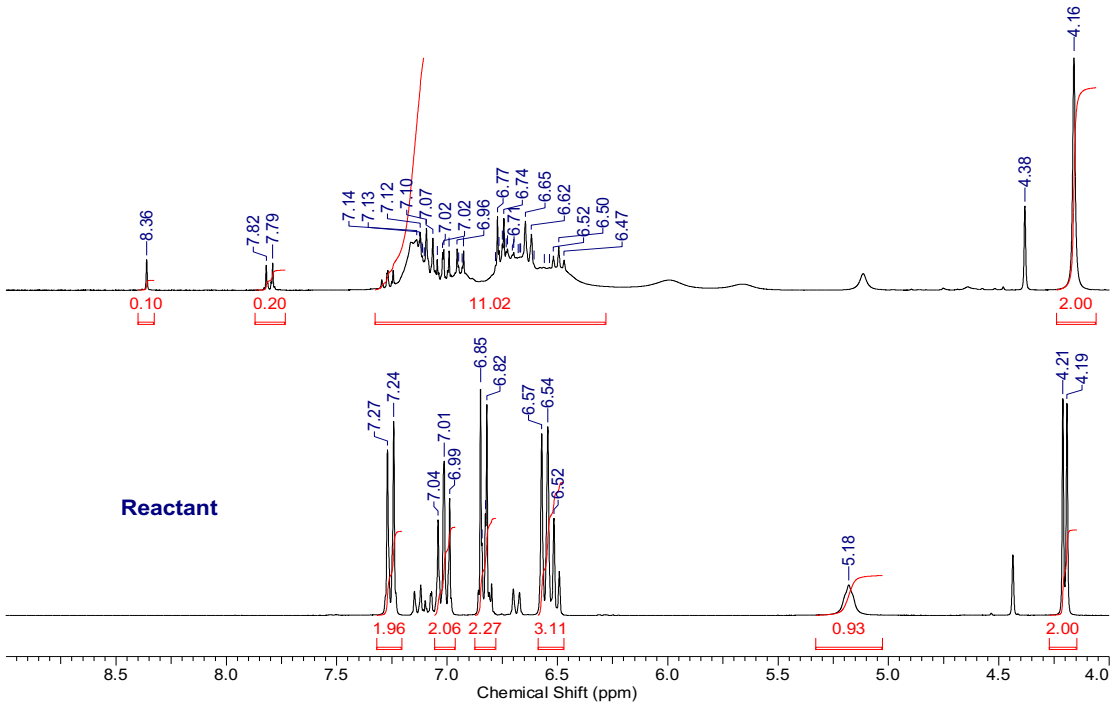


Figure S5 ^{1}H NMR spectrum (300 MHz, THF-d_8) of the reaction between ***N*-PMB-aniline** and LiHMDS.

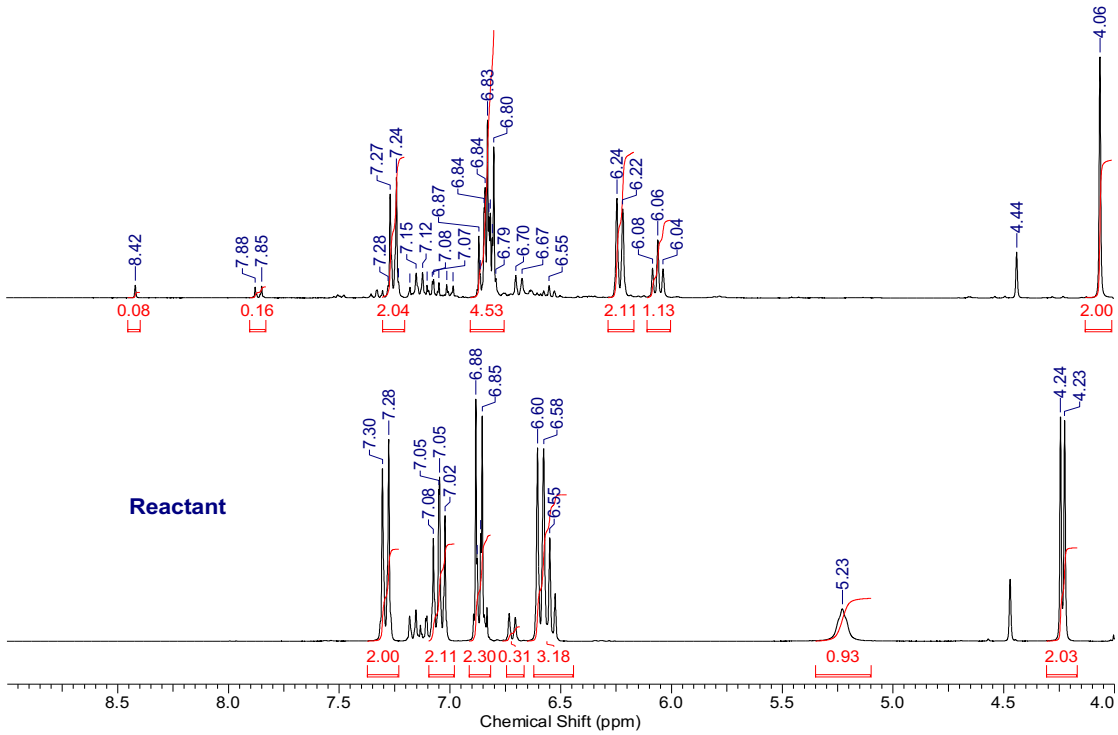


Figure S6 ^{1}H NMR spectrum (300 MHz, THF-d_8) of the reaction between ***N*-PMB-aniline** and KHMDS

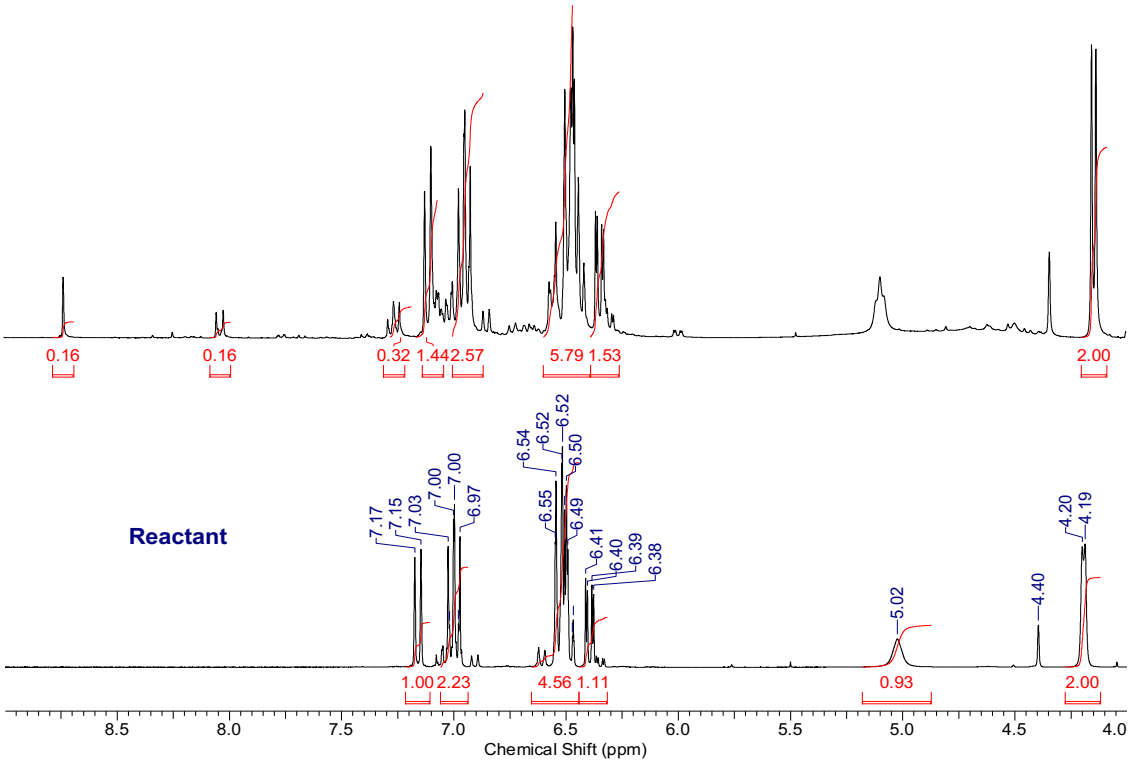


Figure S7 ^{1}H NMR spectrum (300 MHz, THF-d_8) of the reaction between ***N*-DMB-aniline** and LiHMDS

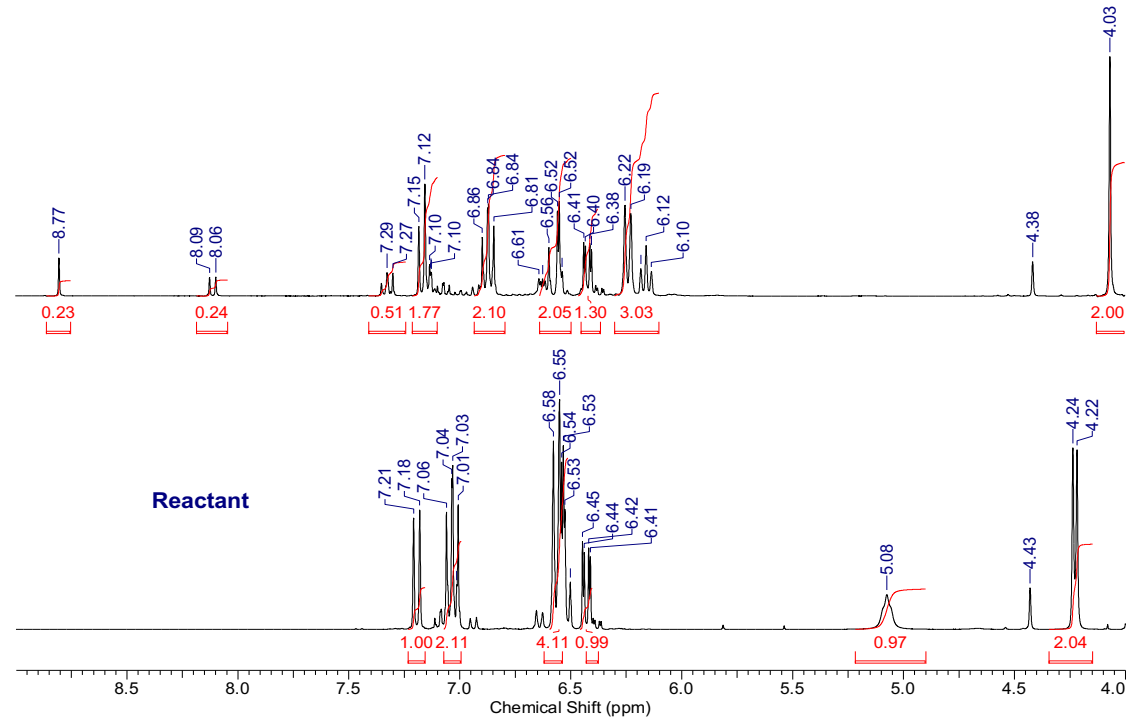


Figure S8 ^{1}H NMR spectrum (300 MHz, THF-d_8) of the reaction between ***N*-DMB-aniline** and KHMDS

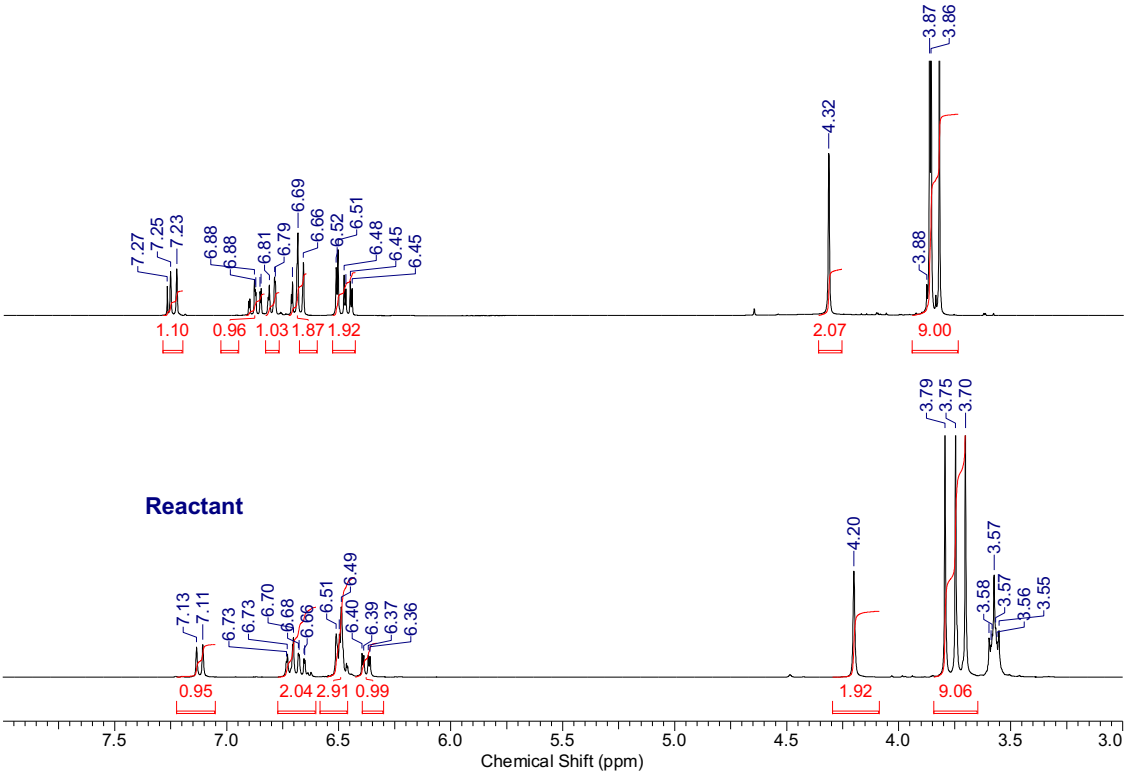


Figure S9 ^{1}H NMR spectrum (300 MHz, THF-d_8) of the reaction between **DMB-*o*-anisidine** and LiHMDS

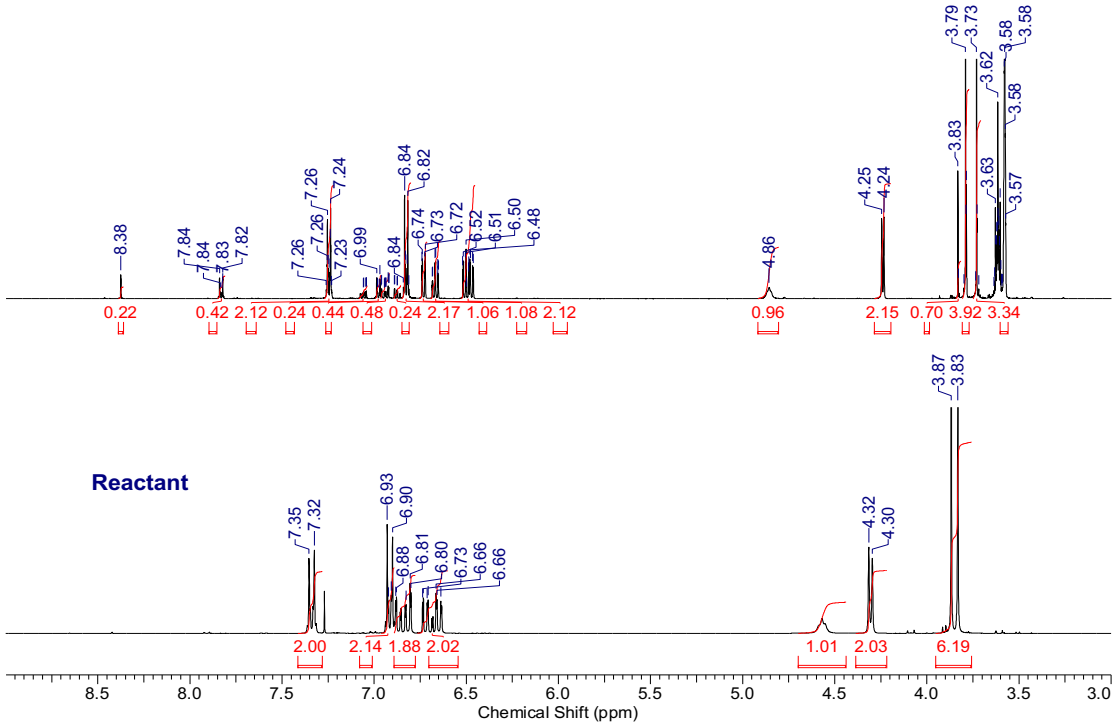


Figure S10 ^{1}H NMR spectrum (300 MHz, THF-d_8) of the reaction between **PMB-*o*-anisidine** and LiHMDS

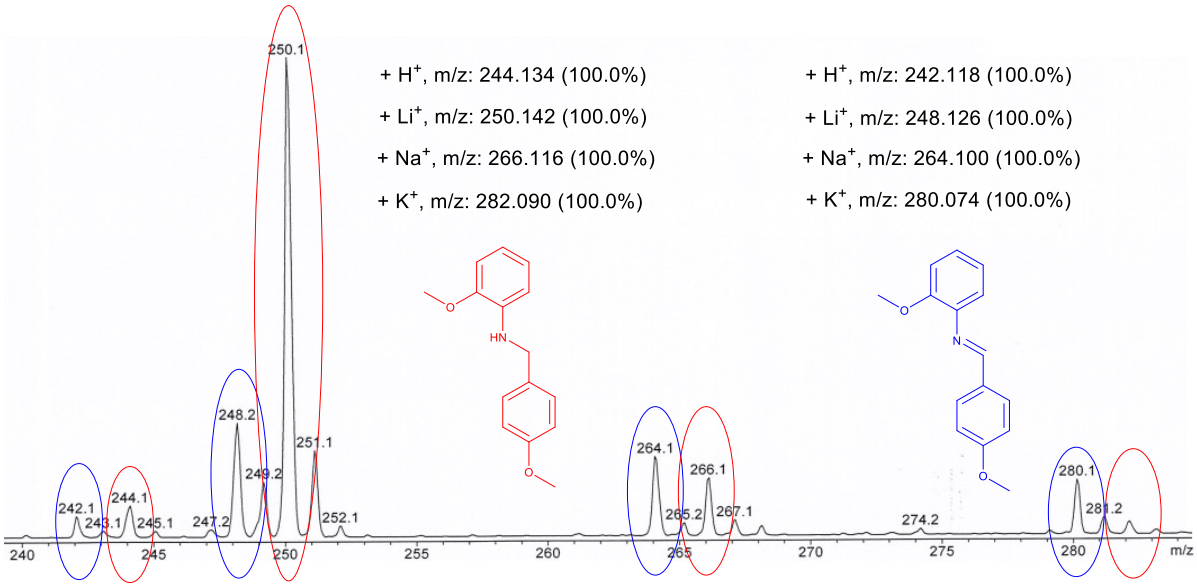


Figure S11 Electro-spray ionization mass spectrometry of the reaction between **PMB-*o*-anisidine** and LiHMDS.

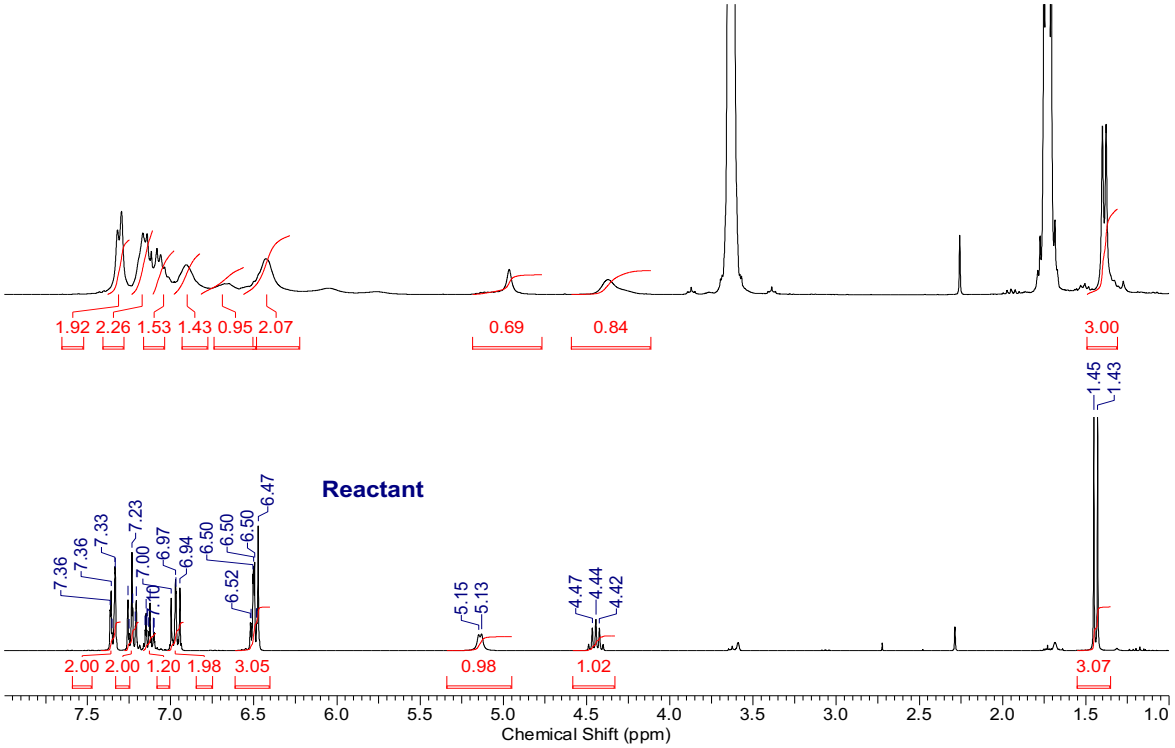


Figure S12 ^{1}H NMR spectrum (400 MHz, THF-d_8) of the reaction between ***N*-(1-phenylethyl)aniline** and LiHMDS

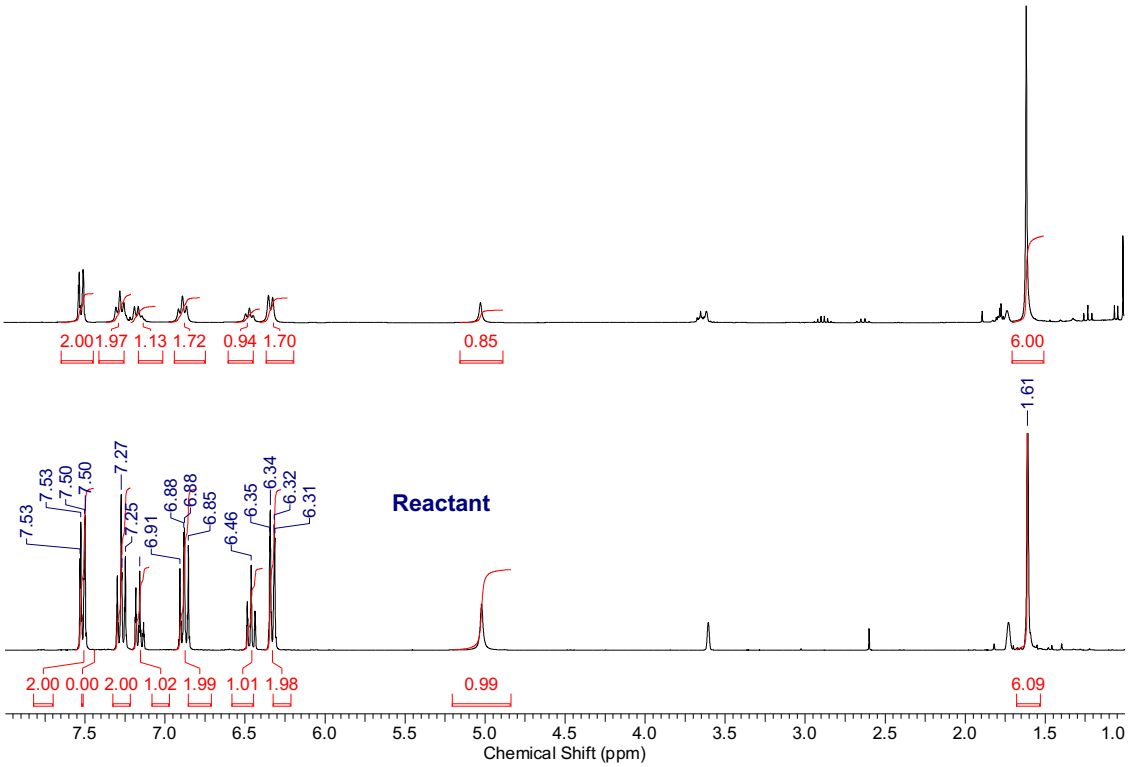


Figure S13 ^{1}H NMR spectrum (400 MHz, THF-d_8) of the reaction between ***N*-(2-phenylpropan-2-yl)aniline** and LiHMDS

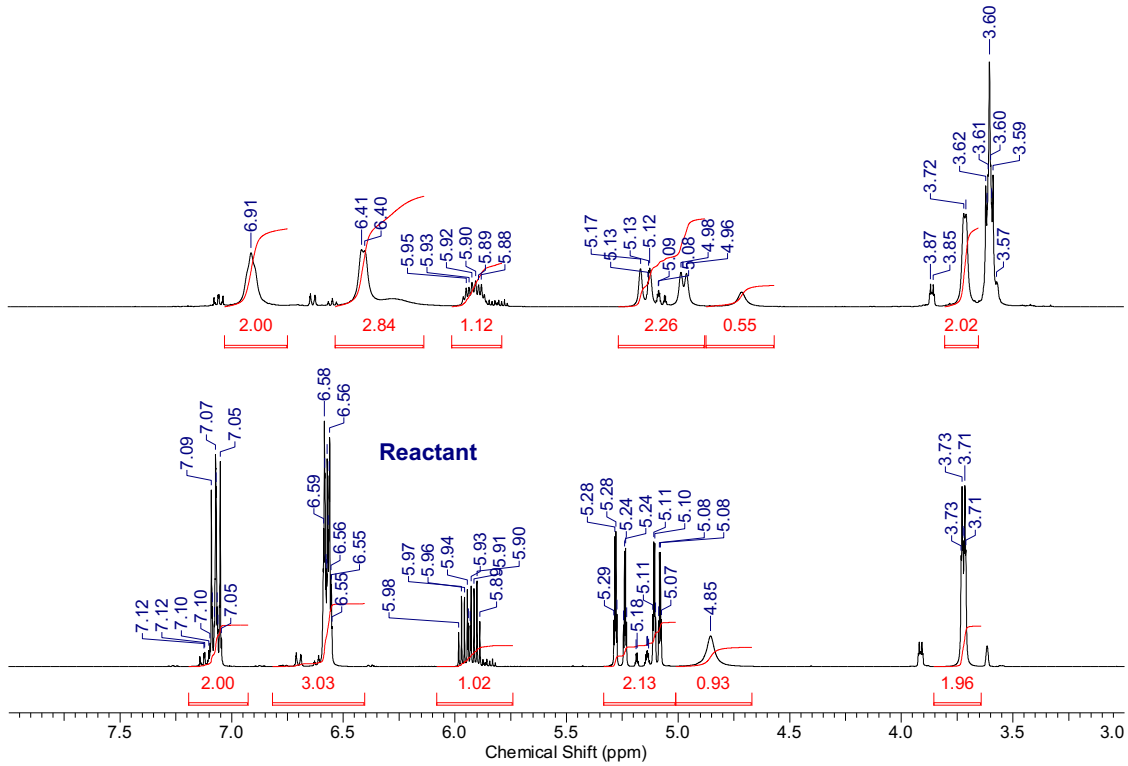


Figure S14 ^{1}H NMR spectrum (400 MHz, THF-d_8) of the reaction between ***N*-allylaniline** and LiHMDS

General procedure for the transamidation reactions

LiHMDS or KHMDS (1 ml, 1 M) was dried on a Schlenk line. *N*-Ethylaniline (0.14 ml, 1.11 mmol) and *N*-Methylbenzanilide (0.235 g, 1.11 mmol) in deuterated THF (1 ml, 1 M) were added to the base and ^{1}H NMR were recorded first every 2 minutes, until the signals were stable, and then the time gaps between measurements were elongated up to 30 minutes. 1H NMR measurements were recorded on a 500 MHz spectrometer.

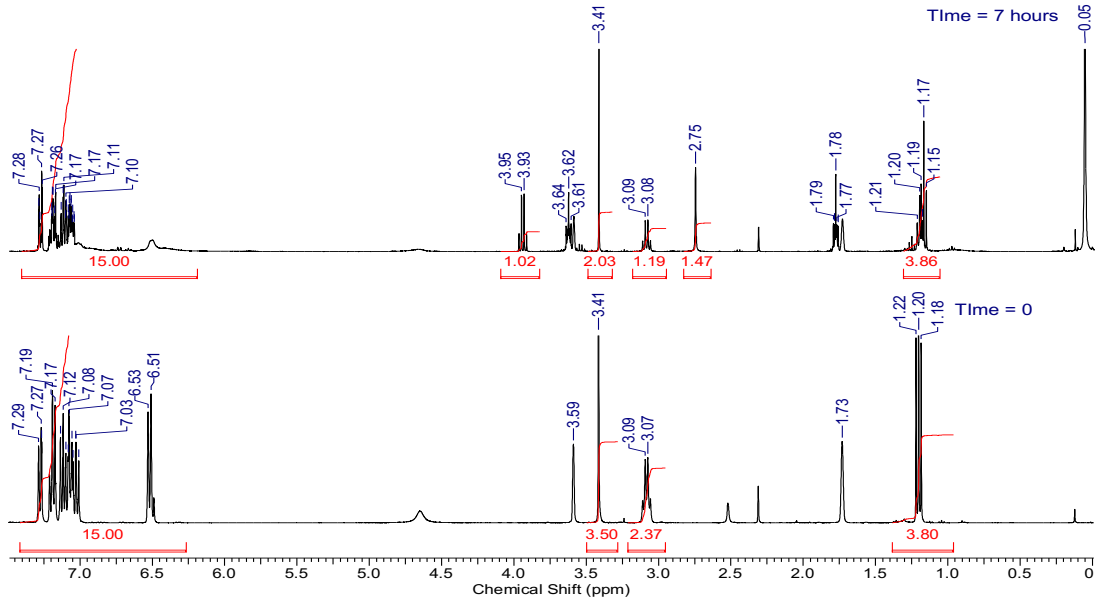


Figure S15 ^{1}H NMR spectrum (500 MHz, THF-d_8) of the reaction between *N*-ethylaniline and *N*-methylbenzanilide and LiHMDS

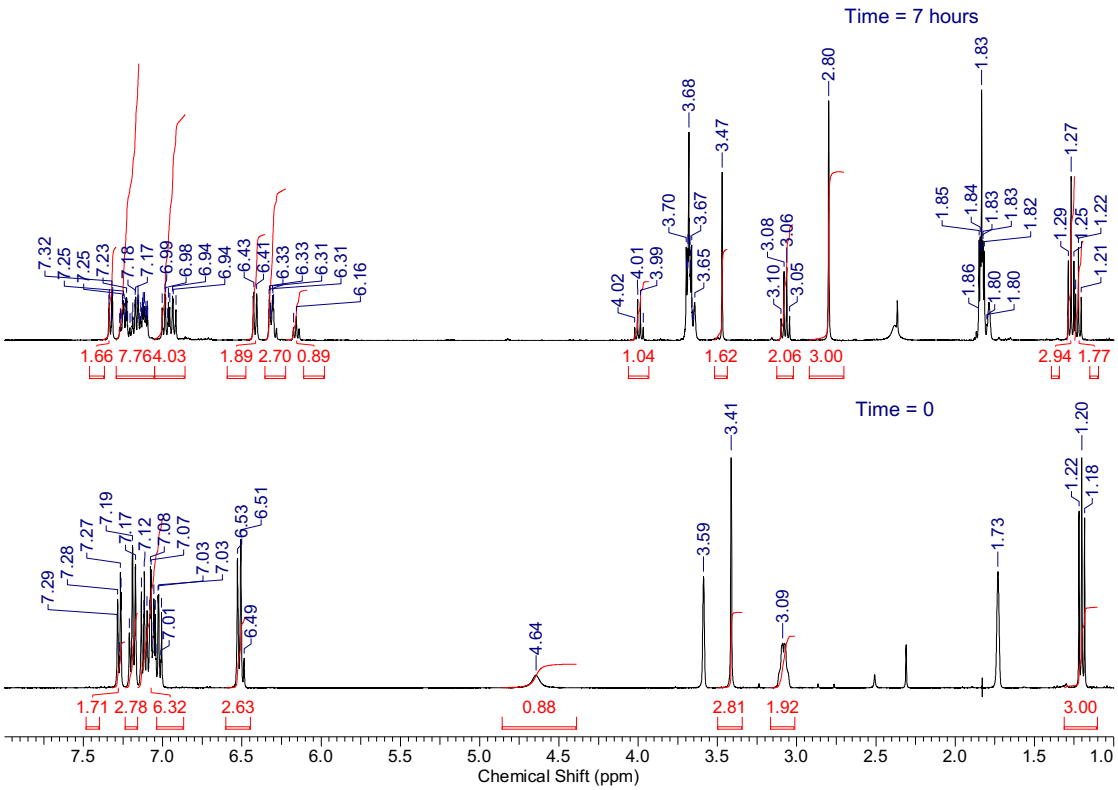


Figure S16 ^{1}H NMR spectrum (500 MHz, THF-d_8) of the reaction between *N*-ethylaniline and *N*-methylbenzanilide and KHMDS

Polymerization of **M2** to **M5**.

All polymers were prepared following the same reaction sequence whereby LiHMDS was cooled to the desired temperature before addition of phenylbenzoate and finally a THF solution of the monomer.

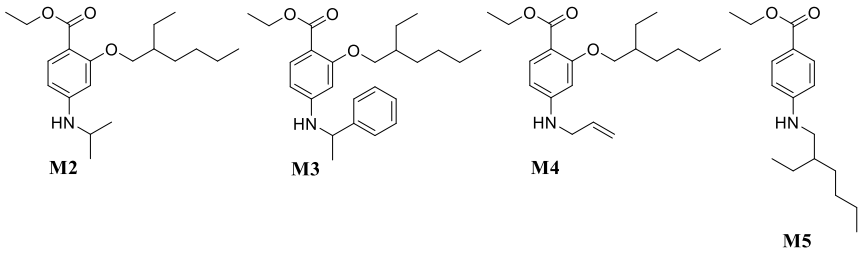


Table SI-1. Molecular weights (GPC, THF) of polymers prepared from **M2** - **M5**

Entry	Monomer	Temperature	LiHMDS (eq.)	Initiator (eq.)	Mn	Mw	PDI
1	**M2**	0°C	1.1	0.01	1200	1200	1.012
2	**M3**	-20°C	1.1	0.01	2500	2900	1.15
3	**M3**	0°C	1.1	0.01	2800	3300	1.14
4	**M4**	0°C	1.1	0.01	1900	2100	1.06
5	**M5**	0°C	1.1	0.01	4800	6600	1.37

[a]GPC was measured in THF using UV detection

Analysis of polymers **M6** to **M11**.

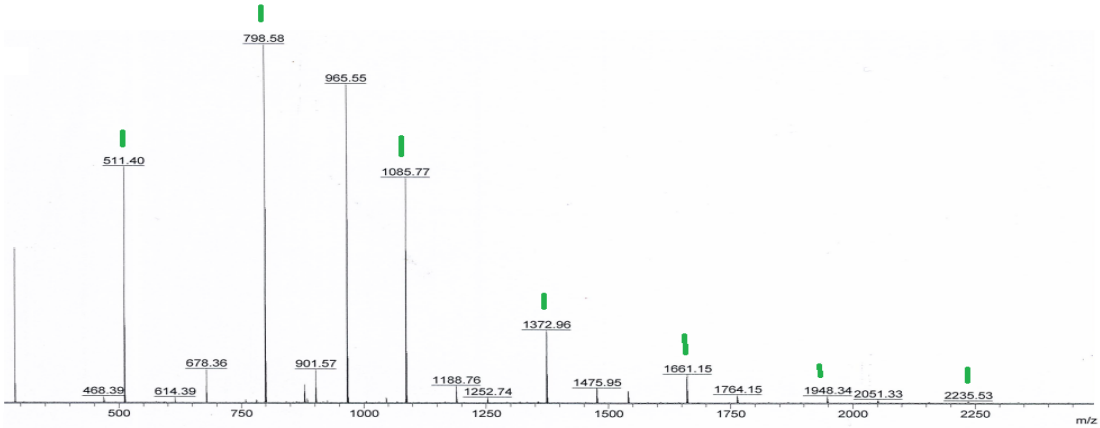


Figure S17 Poly(**M8**) (table 3 entry 3). MALDI-TOF mass spectrum (matrix: DCTB). The green distribution shows the non initiated oligomers.

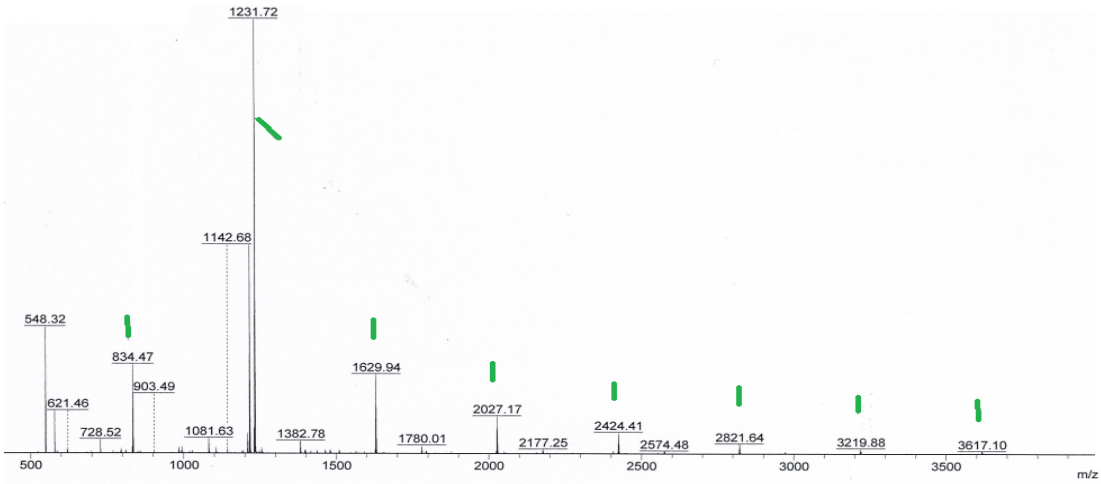


Figure S18 Poly(**M9**) (table 3 entry 4). MALDI-TOF mass spectrum (matrix: DCTB with NaTFA). The green distribution shows the non initiated and ester substituted oligomers.

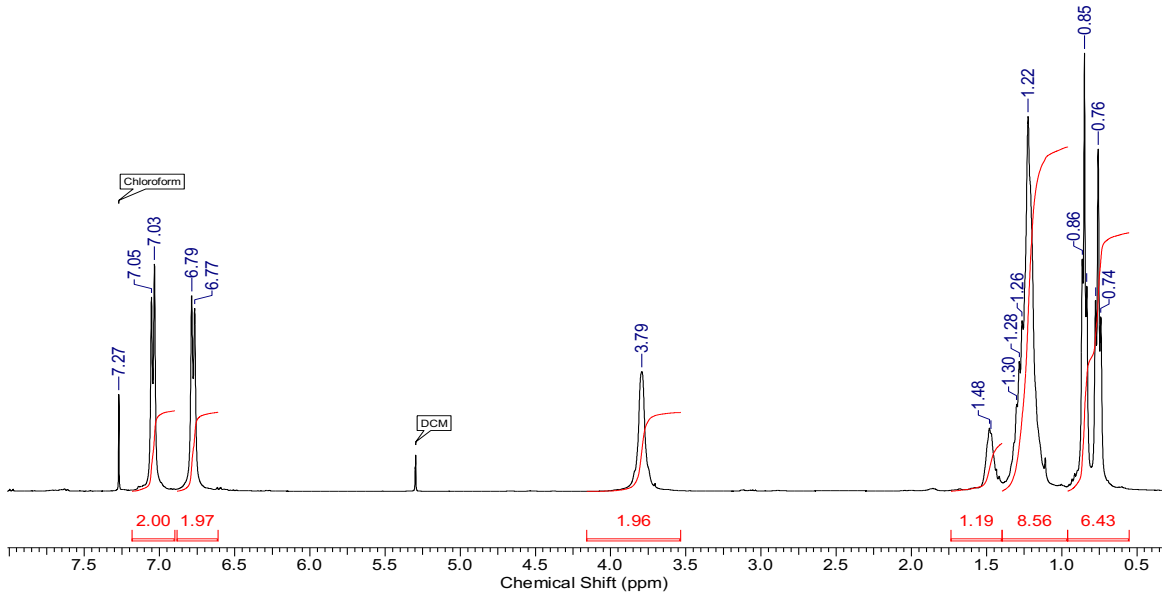


Figure S19 ^{1}H-NMR spectrum (400 MHz, chloroform-d_1) of poly(**M10**) (table 3 entry 7).

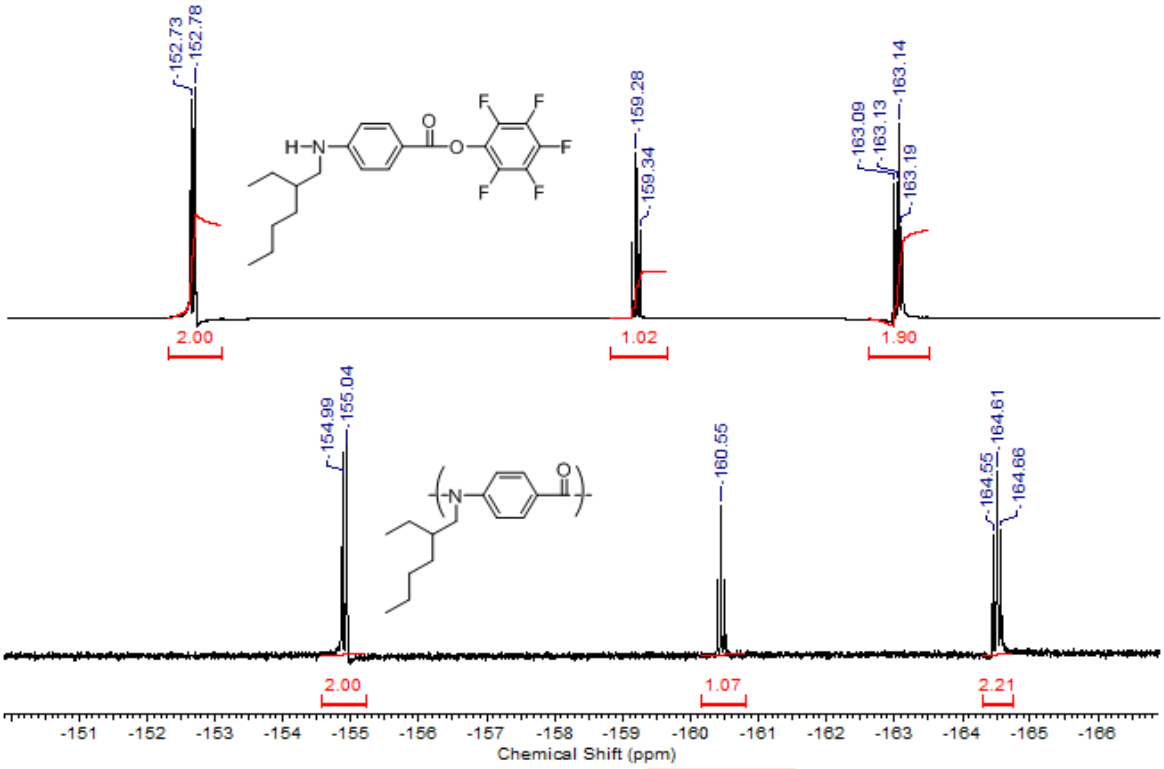


Figure S20 ^{19}F NMR spectra (376 MHz, chloroform-d_1) of the reactant **M10** (top) and the crude poly(**M10**) (table 3 entry 7, bottom). Only traces of the pentafluorophenol are visible, showing ester substitution by LiHMDS.

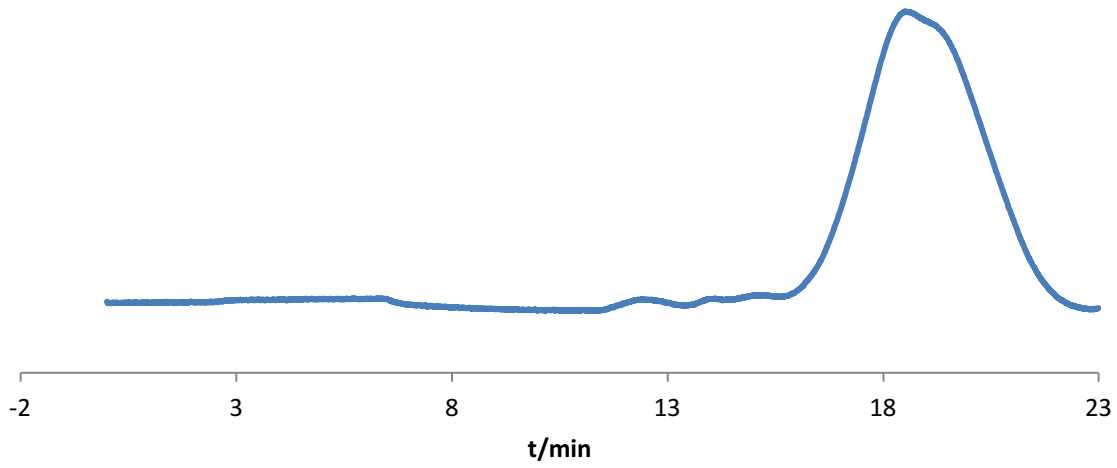


Figure S21 poly(**M10**). Gel permeation chromatography elugram in chloroform. Table 4 entry 4.

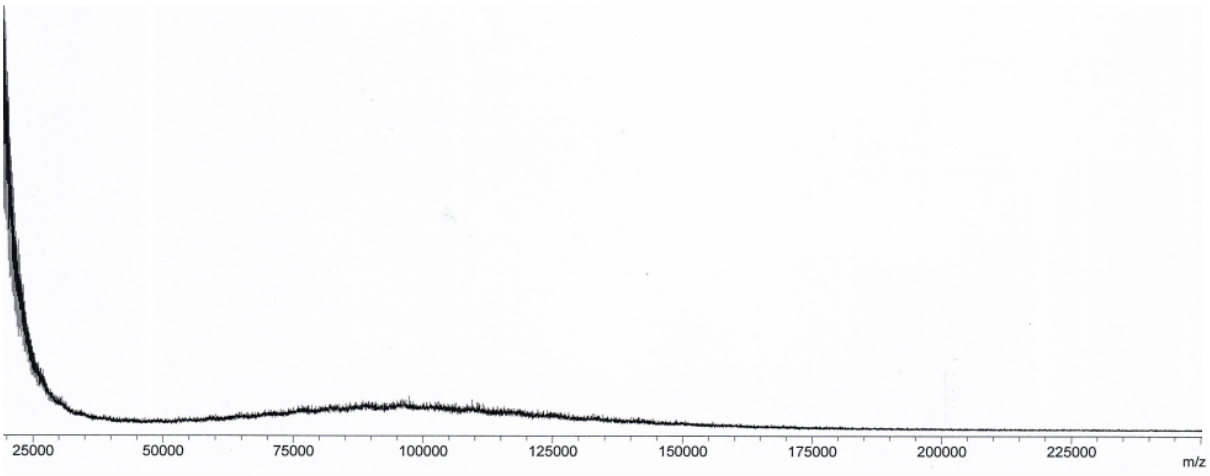


Figure S22 Poly(**M10**) (table 4 entry 5). MALDI-TOF mass spectrum (matrix: DCTB and NaTFA).

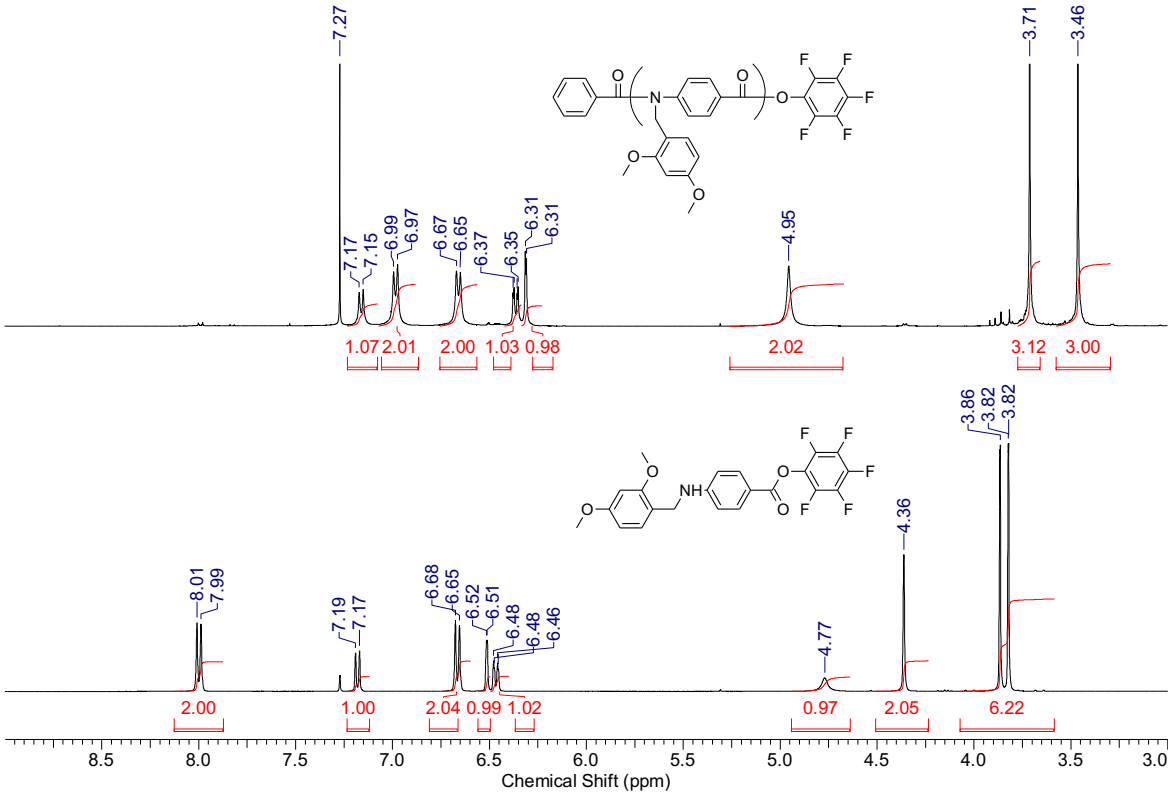


Figure S23 Poly(**M11**). ^{1}H NMR (400 MHz, chloroform-d_1) spectra of the monomer **M11** (bottom) and the polymer (top).

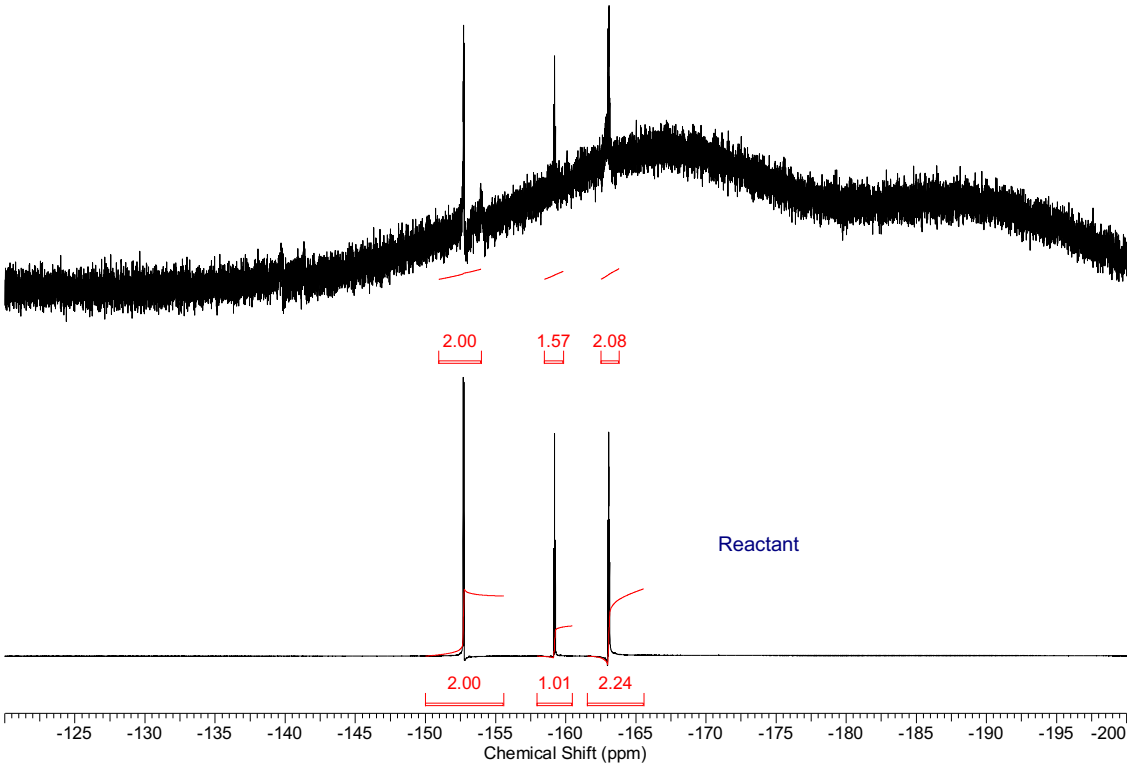


Figure S24 Poly(**M11**). ^{19}F NMR spectra (376 MHz, chloroform-d_1) of the monomer **M11** (bottom) and the polymer (top). The polymer is terminated with PFP ester.

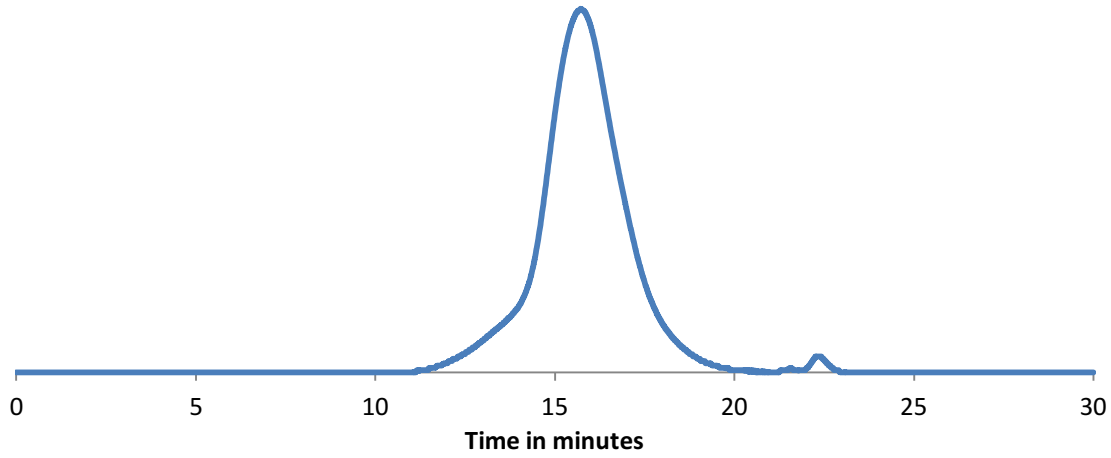
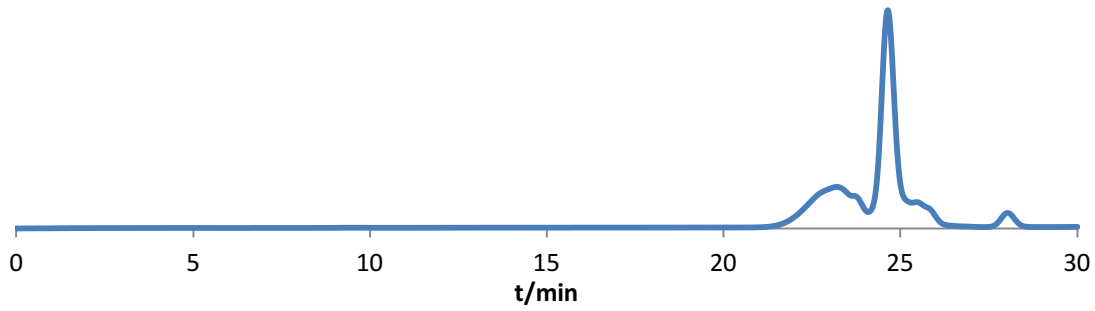
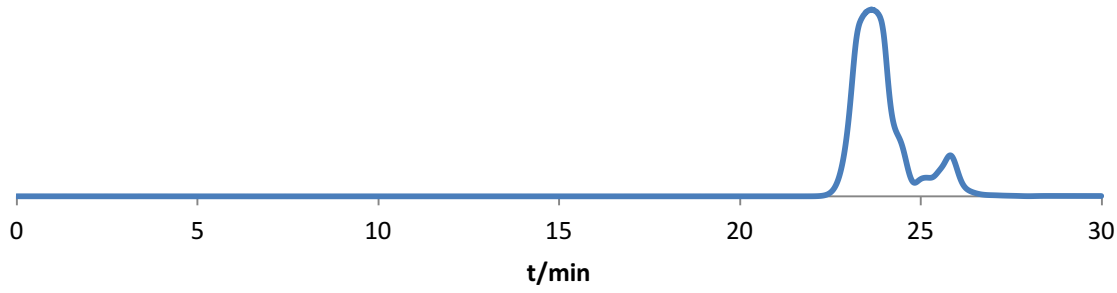


Figure S25 Poly(**M11**). Gel permeation chromatography elugram in chloroform. M_n 44'000, M_w 141'000, PDI 3.2.

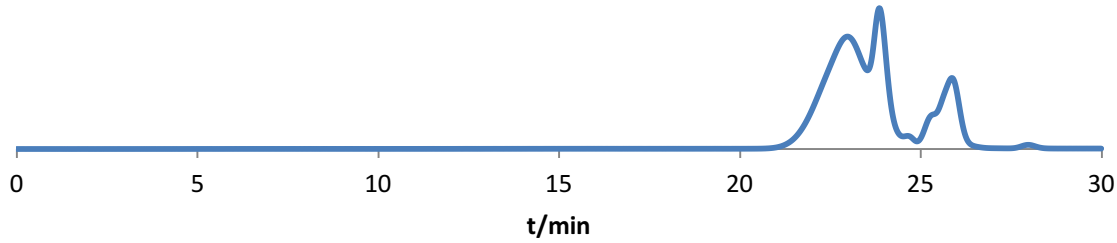
Figures S26. GPC elugrams of table 1, table SI-1, table 3 and table 4.



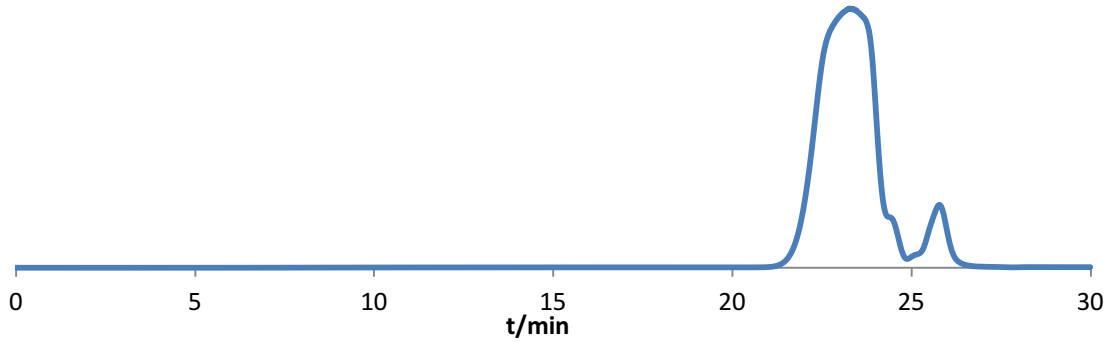
Poly(**M1**) table 1 entry 1 (UV trace of the THF GPC)



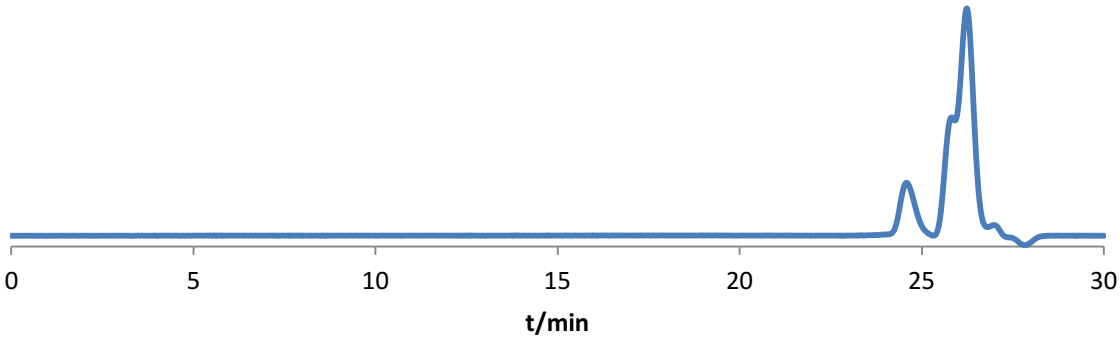
Poly(**M1**) table 1 entry 2 (UV trace of the THF GPC)



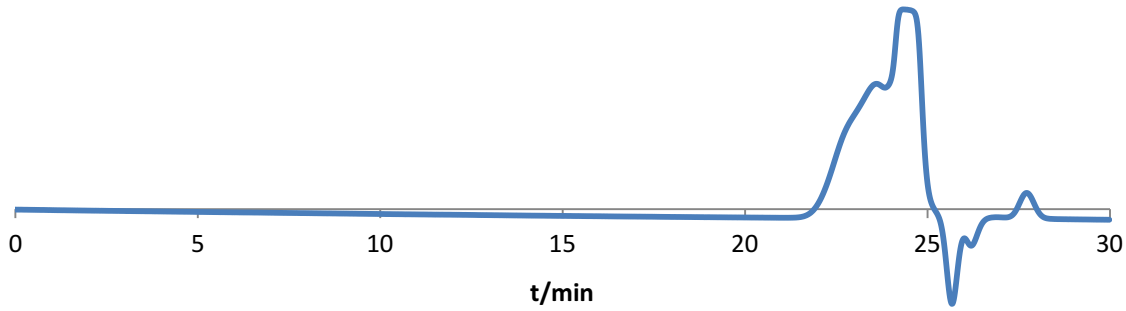
Poly(**M1**) table 1 entry 3 (UV trace of the THF GPC)



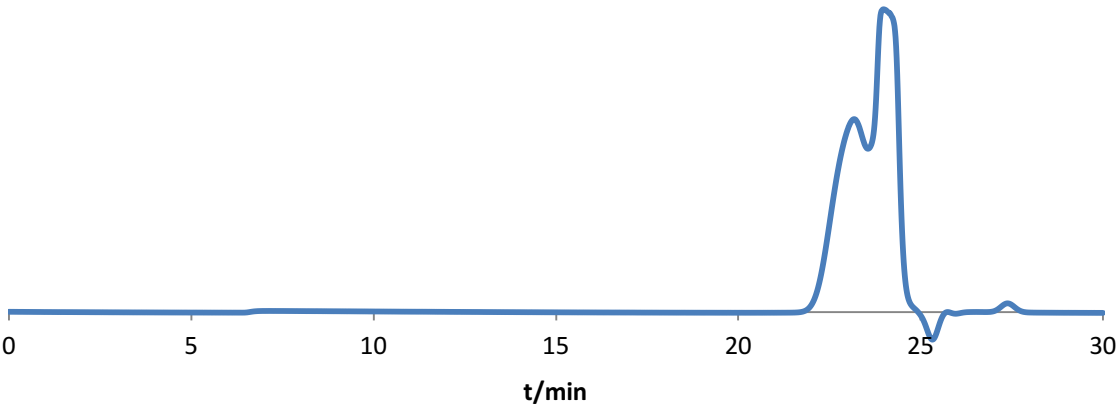
Poly(**M1**) table 1 entry 4 (UV trace of the THF GPC)



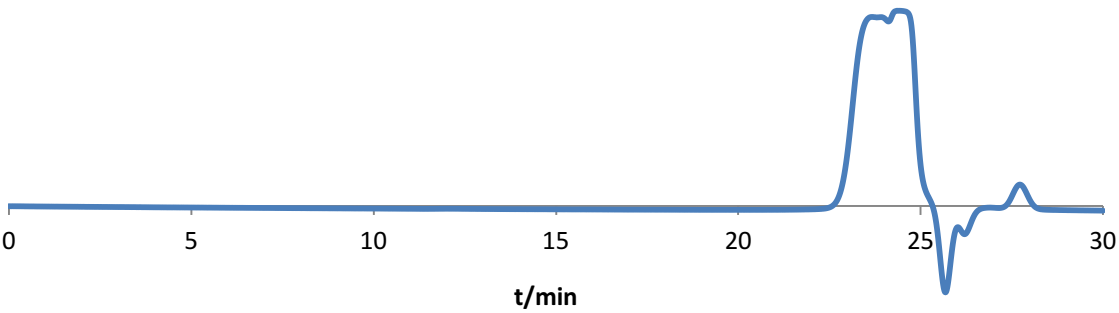
Poly(**M2**) table SI-1 entry 1 (UV trace of the THF GPC)



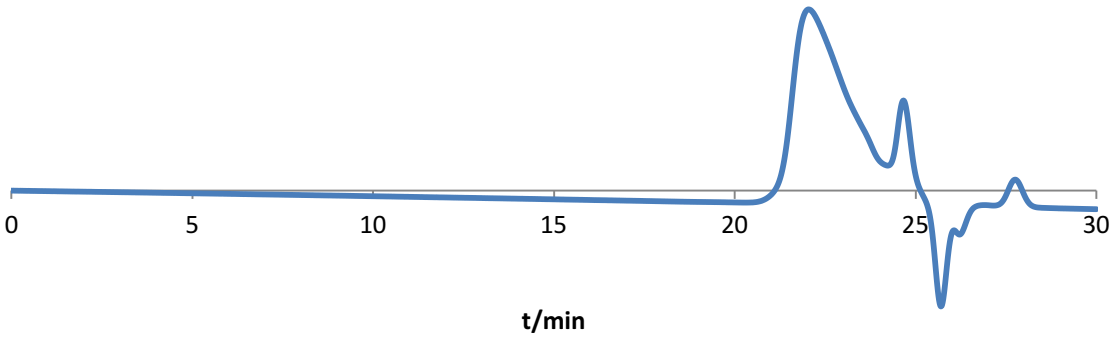
Poly(**M3**) table SI-1 entry 2 (UV trace of the THF GPC)



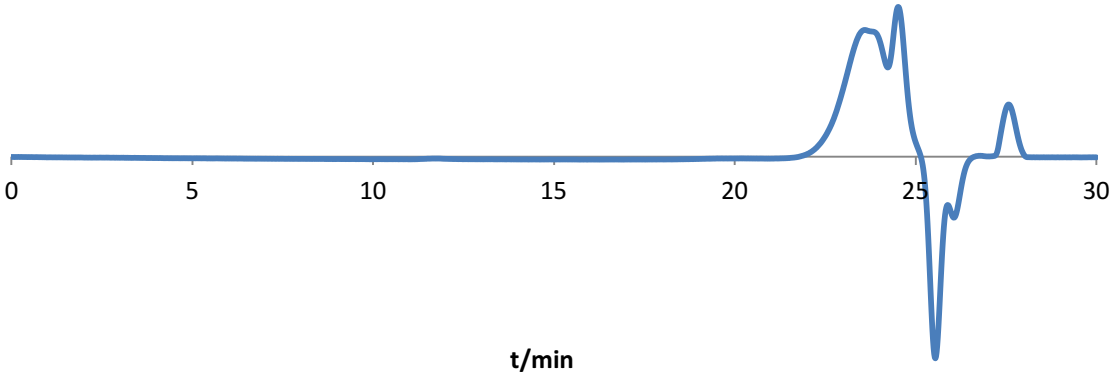
Poly(**M3**) table SI-1 entry 3 (UV trace of the THF GPC)



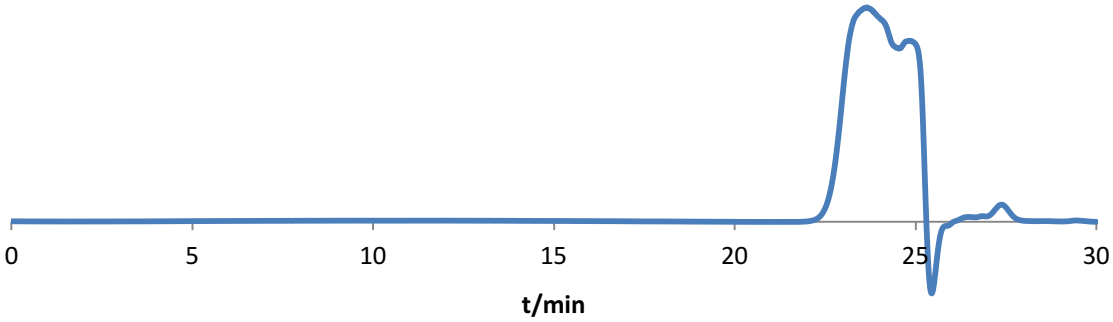
Poly(**M4**) table SI-1 entry 4 (UV trace of the THF GPC)



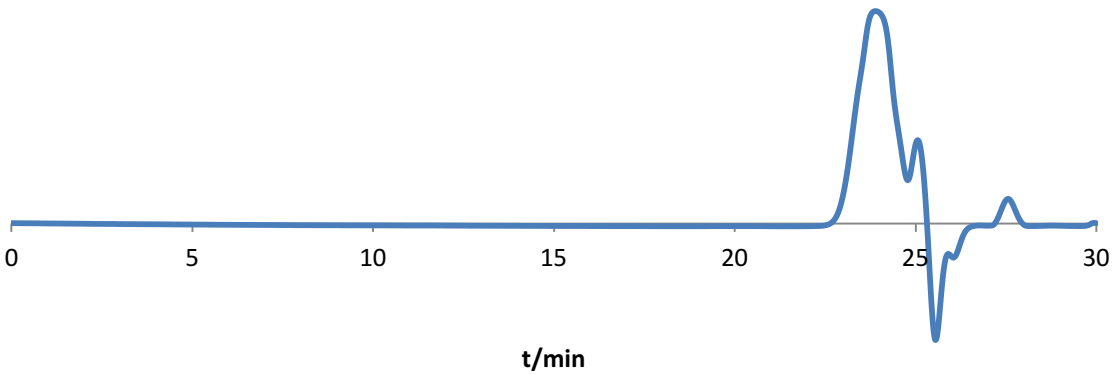
Poly(**M5**) table SI-1 entry 5 (UV trace of the THF GPC)



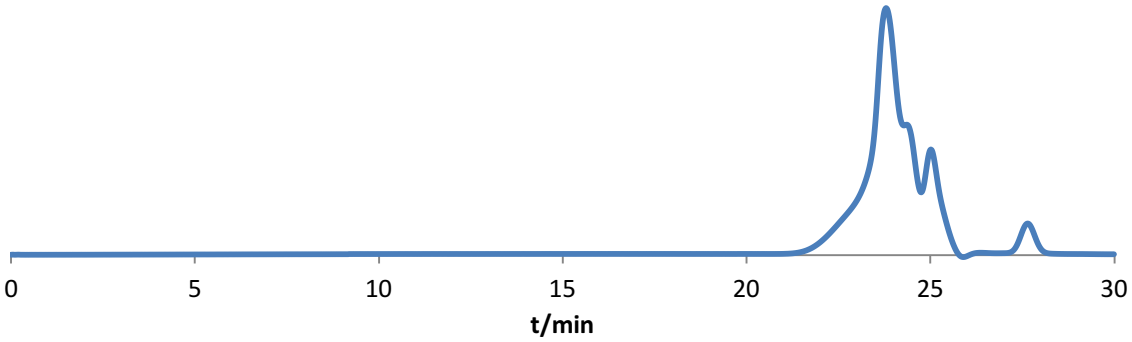
Poly(**M6**) table 3 entry 1 (UV trace of the THF GPC)



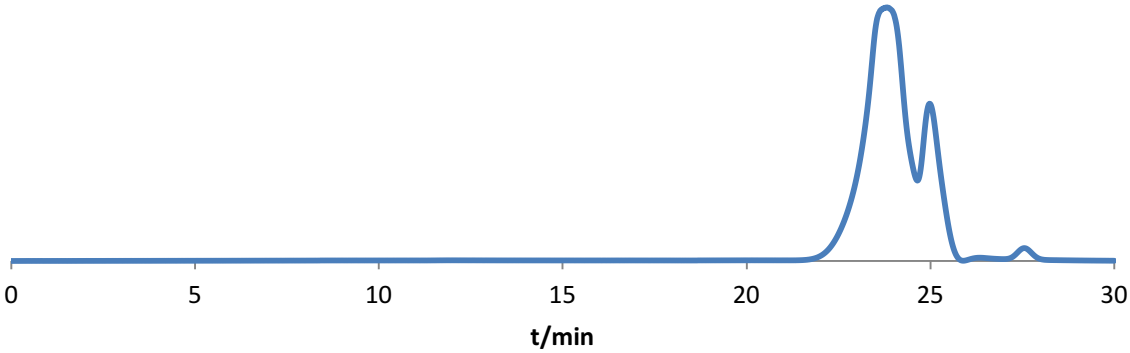
Poly(**M7**) table 3 entry 2 (UV trace of the THF GPC)



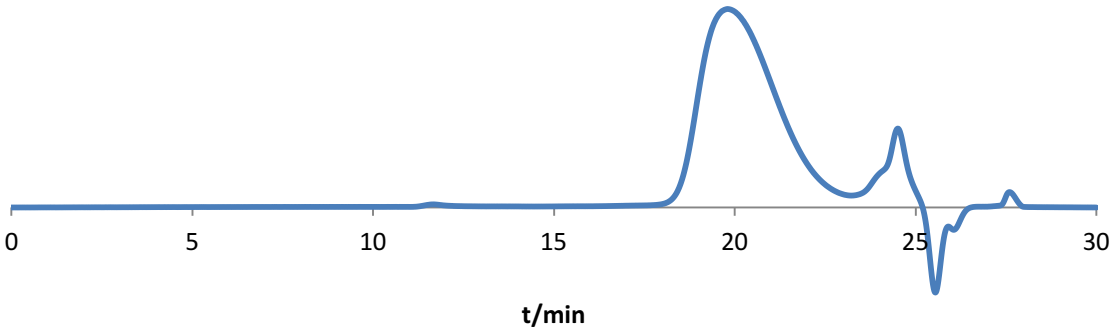
Poly(**M8**) table 3 entry 3 (UV trace of the THF GPC)



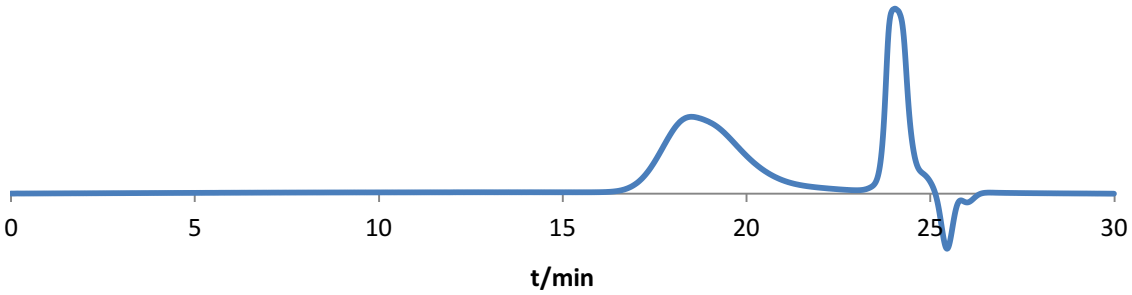
Poly(**M9**) table 3 entry 4 (UV trace of the THF GPC)



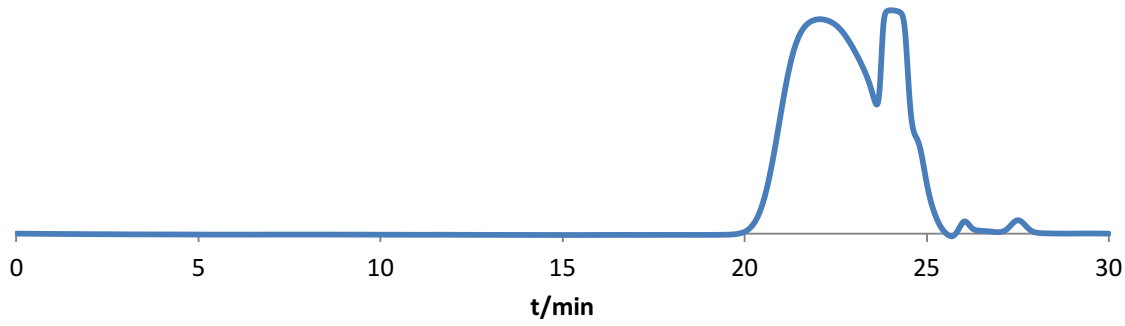
Poly(**M9**) table3 entry 5 (UV trace of the THF GPC)



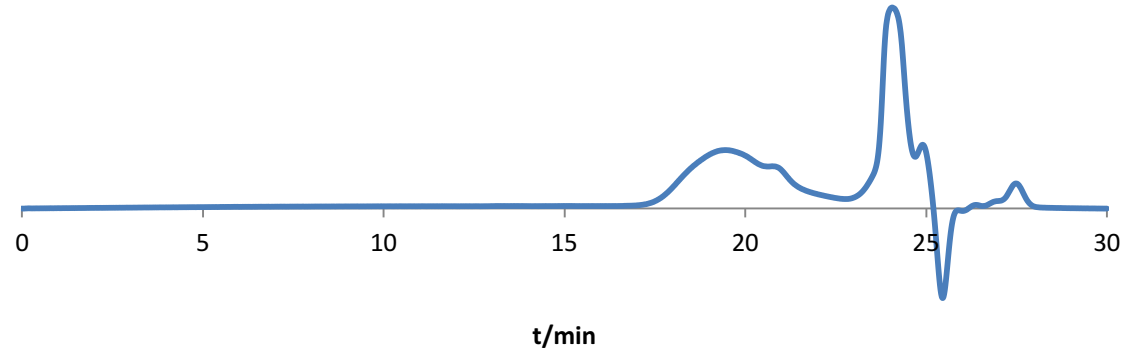
Poly(**M10**) table 3 entry 6 (UV trace of the THF GPC)



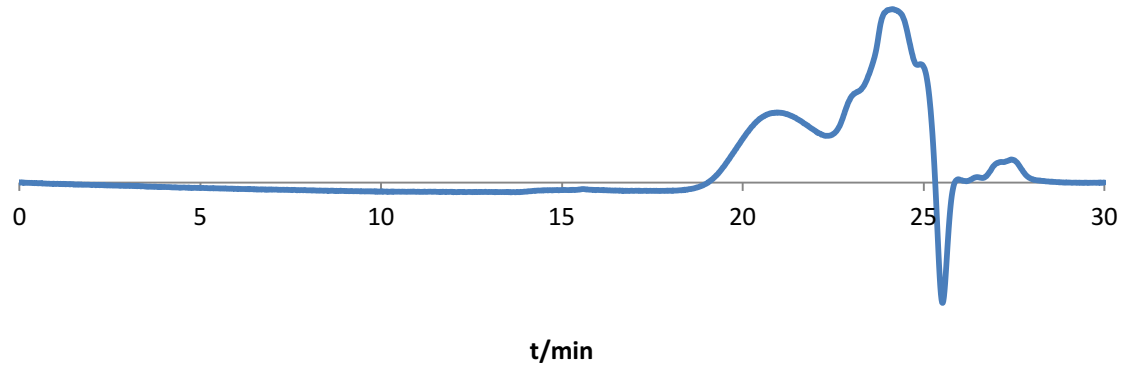
Poly(**M10**) table 3 entry 7 (UV trace of the THF GPC)



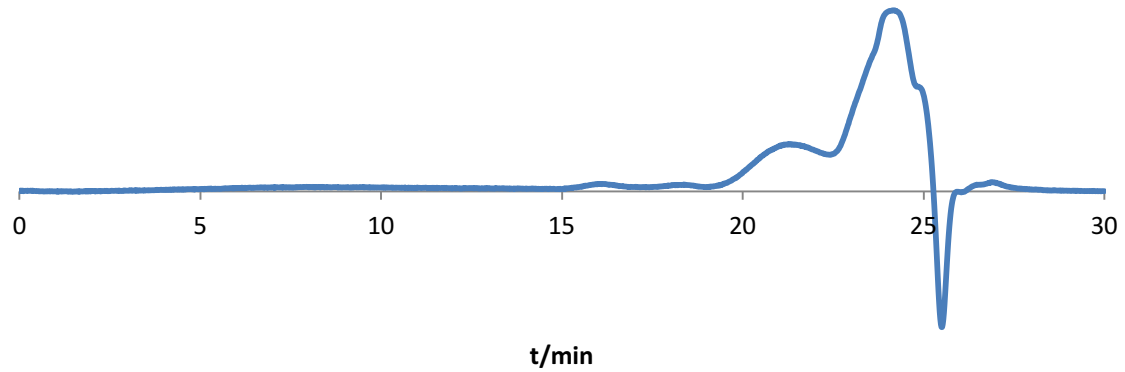
Poly(**M10**) table 3 entry 8 (UV trace of the THF GPC)



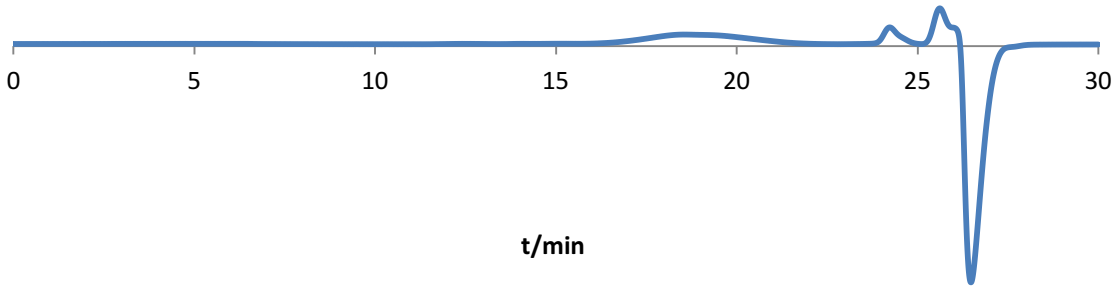
Poly(**M10**) table 4 entry 1 (UV trace of the THF GPC)



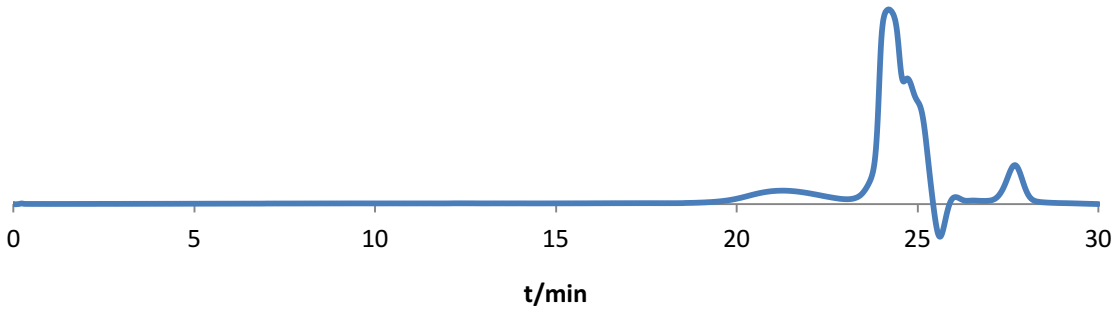
Poly(**M10**) table 4 entry 2 (UV trace of the THF GPC)



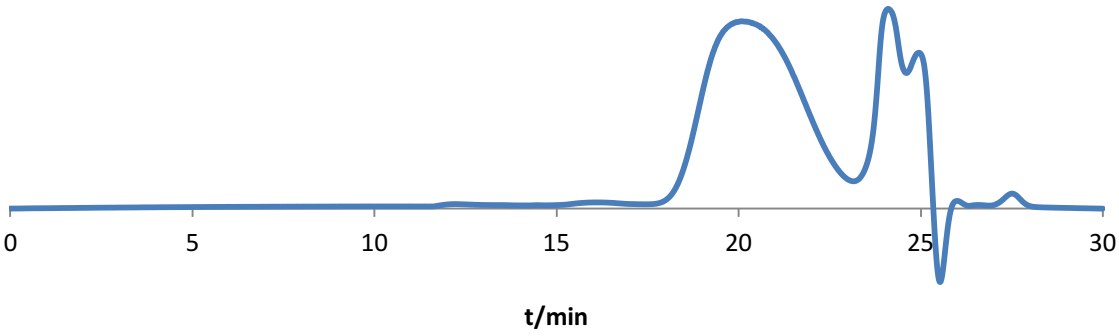
Poly(**M10**) table 4 entry 3 (UV trace of the THF GPC)



Poly(**M10**) table 4 entry 4 (RI trace of the THF GPC)



Poly(**M10**) table 4 entry 5 (UV trace of the THF GPC)



Poly(**M10**) table 4 entry 6 (UV trace of the THF GPC)