Side-Chain Supramolecular Polymers Employing Conformer Independent Triple Hydrogen Bonding Arrays

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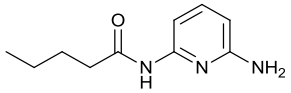
SUPPORTING INFORMATION

General Points All reagents were purchased from commercial sources and were used without further purification. All non-aqueous procedures were performed under an inert atmosphere of nitrogen or argon. Where anhydrous solvents were required, $CHCl_3$ was freshly distilled from calcium chloride under a nitrogen atmosphere. Triethylamine was distilled from calcium hydride and stored over potassium hydroxide pellets prior to use. THF was either freshly distilled from sodium benzophenone ketyl radical or obtained from an Innovative Technology Inc. PureSolv® solvent purification system. Anhydrous acetone was obtained from the latter in all cases. H_2O refers to deionised H_2O. Methyl methacrylate and styrene were freshly purified by vacuum distillation from calcium hydride and stored over 4Å molecular sieves at 4ºC in the dark. Azobutyronitrile (AIBN) was recrystallized twice from MeOH and stored at –18ºC in the dark prior to use. Petroleum ether refers to the fraction with boiling range 40 – 60ºC. Thin layer chromatography was carried out on Merck silica gel 60F254 pre-coated aluminium foil sheets. The compounds were visualized using UV light (254 nm) and the stain specified where used. Flash column chromatography was carried out at medium pressure using slurry packed Fluka silica gel (SiO_2), 35 – 70 μm, 60 Å, with the specified eluent. Melting points were determined using a Griffin D5 variable temperature apparatus and are uncorrected. CHN elemental analyses were performed by the University of Leeds elemental analysis service and were determined using a Carlo Erba Elemental Analyser MOD 1106 instrument. NMR spectra were obtained using Bruker DMX500, Bruker DMX400 or Bruker AMD300 spectrometers operating at 500 MHz, 400 MHz or 300 MHz respectively for ^1H spectra and 125 MHz, 100 MHz and 75 MHz respectively for ^{13}C NMR as stated. All spectral data reported was acquired at 295 K. Chemical shifts (δ) are quoted in part per million (ppm), using the residual solvent peak as an internal standard (e.g. δH 7.26 and δC 77.00 for $CDCl_3$). Coupling constants (*J*) are reported in Hz to an accuracy of 0.1 Hz. The abbreviations used to denote 1H NMR multiplicity are as follows: s, singlet; d, doublet; t,

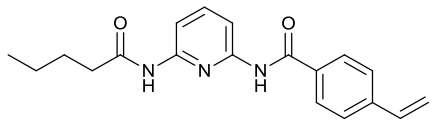
triplet; q, quartet; m, multiplet; br, broad; app, apparent. Abbreviations used to describe 1H NMR assignments are as follows: Ar, aryl; (o), ortho; (m), meta; (p), para. Signal assignment was aided by analysis of DEPT, COSY, NOESY, HMBC, HSQC and variable–temperature ^{1}H NMR experiments where necessary. IR spectra were obtained using Perkin–Elmer FTIR spectrometer. Mass spectra were recorded on a Bruker Hystar Compass LC-MS 1200 using electrospray ionisation (ESI) and high resolution mass spectra were recorded on a Bruker Daltonics micrOTOF spectrometer using electrospray ionisation (ESI).

***N*-(6-aminopyridin-2-yl)pentanamide 9**



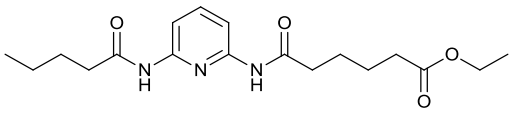
To a stirred solution of 2,6-diaminopyridine **7** (15.0 g, 137 mmol) in THF (150 mL) and triethylamine (14.1 mL, 101 mmol), was added pentanoylchloride 8 (10.9 mL, 91.5 mmol) dropwise *via* cannula over 5 minutes at 0°C under nitrogen atmosphere. The solvent was removed under reduced pressure to provide a viscous yellow oil. The oil was dissolved in $CHCl_3$ (30 mL) and washed with H_2O (5 × 100 mL). The organic portion was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (SiO_2, 3:97 MeOH–$CHCl_3$) of the resulting residue provided the title compound (15.5 g, 80.0 mmol, 87%) as a pale yellow solid; R_F: 0.45 (3:97 MeOH–$CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.72 (1H, br s, NHCO), 7.54 (1H, d, *J* = 7.8 Hz, pyridyl-H), 7.44 (1H, app t, *J* = 8.1 Hz, pyridyl-H), 6.23 (1H, d, *J* = 7.8 Hz, pyridyl-H), 4.30 (2H, br s, NH_2), 2.34 (2H, t, *J* = 7.6 Hz, $CH_3CH_2CH_2CH_2$), 1.69 (2H, dt, *J* = 7.3, 7.6 Hz, $CH_3CH_2CH_2$), 1.38 (2H, m, CH_2CH_3), 0.94 (3H, t, *J* = 7.5 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.1, 157.4, 150.2, 140.7, 104.5, 103.7, 37.9, 27.9, 22.7, 14.2; ν_{max}/cm^{-1} (solid state): 3412, 3328, 2962, 2871, 2453, 2261, 1967, 1846, 1669, 1527, 1436; ESI-HRMS found m/z 194.1288 $[M + H]^+$ $C_{10}H_{16}N_3O$ requires 194.1293.

2-Pentanoylamido-6-(4-vinylphenylamido)pyridine 6



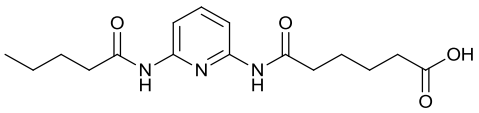
2-pentanoylamido-6-aminopyridine **9** (2.5 g, 12.9 mmol), 4-vinylbenzoic acid **10** (2.3 g, 15.5 mmol) and 4-dimethylaminopyridine (1.89 g, 15.5 mmol) were added to CH_2Cl_2 (80 mL) under nitrogen. The reaction mixture was cooled 0°C and left stirring for 10 minutes. EDCI was added to the reaction mixture and left stirring overnight. This yielded a yellow solution to which was added CH_2Cl_2 (50 mL), washed with 1M HCl (80 mL), $NaHCO_3$ (80 mL) and brine (80 mL). The organic extracts were then dried with anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography (SiO_2, gradient elution; 100:0 - 90:10 DCM: Ethyl acetate) was used to isolate the monomer (1.41 g, 73%) as a white solid; (Found: C, 70.3; H, 6.45; N, 12.95; $C_{19}H_{21}N_3O_2$ requires C, 70.57; H, 6.55; N, 12.99); R_F: 0.30 (90:10 DCM-Ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.25 (1H, s, CONH); 8.05 (1H, d, J = *6* Hz, ArCH), 7.95 (1H, d, J = *9* Hz, ArCH), 7.85 (2H, dd, *J* = 6 Hz, 3 Hz, ArCH), 7.74 (1H, t, *J* = 9 Hz, ArCH) , 7.63 (1H, s, CONH), 7.50 (2H, d, *J* = 9 Hz, ArCH), 6.76 (1H, dd, *J* = 10.9 Hz, 6.7 Hz, CH_2=C<u>H</u>), 5.87 (1H, d, *J* = 17.6 Hz, C<u>H$_2$</u>=CH), 5.4 (1H, d, *J* = 10.9 Hz, C<u>H$_2$</u>=CH), 2.38 (2H, t, *J* = 7.4 Hz, $CH_3CH_2CH_2C$<u>H$_2$</u>), 1.71 (2H, sept, *J* = 7.4 Hz, CH_3CH_2C<u>H$_2$</u>CH_2), 1.41 (2H, sext, *J* = 7.4 Hz, CH_3C<u>H$_2$</u>CH_2), 0.95 (3H, t, *J* = 7.4 Hz, C<u>H$_3$</u>CH_2CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.9, 165.4, 150.0, 141.9, 141.3, 136.2, 133.5, 127.9, 127.0, 117.0, 110.1, 110.0, 38.0, 27.8, 22.7, 14.2; ν_{max}/cm^{-1} = 3736, 3336, 2955, 1654, 1469, 1309, 798; ESI-MS *m/z* = 324 $[M+H]^+$.

Ethyl 6-Oxo-6-(6-pentanamidopyridin-2-ylamino)hexanoate (11a)



To a stirring solution of 6-ethoxy-6-oxohexanoic acid **10** (0.520 g, 1.24 mmol) in $CHCl_3$ (15 mL) was added *N*-(6-aminopyridin-2-yl)pentanamide **9** (0.304 g, 2.43 mmol) and 4-dimethylaminopyridine (0.317 g, 2.58 mmol) under nitrogen atmosphere. The reaction mixture was cooled to 0°C for 10 minutes. EDCI (0.510 g, 2.60 mmol) was then added and the reaction was allowed to warm to room temperature and stirred for 16 hr. The resulting solution was concentrated under reduced pressure and the remaining residue was purified *via* column chromatography (SiO_2, 3:7 EtOAc–CH_2Cl_2) to provide the target material (0.509 g, 1.45 mmol, 61%) as a fluffy colourless powder; R_F: 0.40 (97:3 CH_2Cl_2–MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.83 (1H, d, *J* = 8.0 Hz, pyridyl-H), 7.80 (1H, s, NH), 7.63 (1H, app t, *J* = 8.1 Hz, pyridyl-H), 7.47 (1H, d, *J* = 8.1 Hz, pyridyl-H),7.46 (1H, s, NH), 4.07 (2H, q, *J* = 7.1 Hz, $CH_3C\underline{H}_2O$), 2.33 – 2.29 (6H, m, $CH_2OC(O)C\underline{H}_2$, $CH_2OC(O)C\underline{H}_2CH_2CH_2CH_2$, $C\underline{H}_2CH_2CH_2CH_3$), 1.72 – 1.61 (6H, m, $CH_2OC(O)CH_2C\underline{H}_2$, $CH_2OC(O)CH_2C\underline{H}_2CH_2$, $CH_2C\underline{H}_2CH_2CH_3$), 1.34 (2H, m, $CH_2C\underline{H}_2CH_3$), 1.19 (3H, t, *J* = 7.1 Hz, $C\underline{H}_3CH_2O$), 0.88 (3H, t, *J* = 7.3 Hz, $CH_2CH_2C\underline{H}_3$); ^{13}C NMR (75 MHz, CDCl3) δ: 173.7, 171.9, 171.3, 149.9, 149.7, 141.2, 109.8, 109.7, 60.8, 38.0, 37.7, 34.3, 27.8, 25.1, 24.7, 22.7, 14.6, 14.2; ν_{max}/cm^{-1} (solid state): 3327, 2957, 2871, 1720, 1692, 1663, 1587, 1516; ESI-HRMS found m/z 350.2074 $[M + H]^+$ $C_{18}H_{28}N_3O_4$ requires 350.2080.

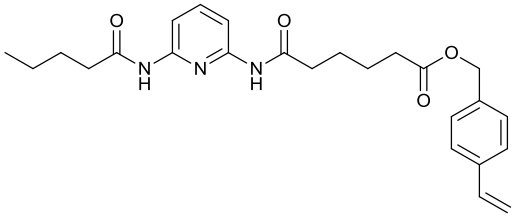
6-Oxo-6-(6-pentanamidopyridin-2-ylamino)hexanoic acid 11



A solution of ethyl 6-oxo-6-(6-pentanamidopyridin-2-ylamino)hexanoate (**11a**) (0.390 g, 1.11 mmol) in EtOH (14 mL) and THF (1mL) was added in one portion to a stirring sodium

hydroxide solution (15 mL, pH 13) at room temperature. The reaction mixture was stirred for 16 hr before neutralizing to pH 7 with 0.1 M HCl solution. The reaction mixture was then poured onto EtOAc (20 mL) and extracted. The organic portion was collected and washed with H_2O (3 × 50 mL) and dried over Na_2SO_4. The organic solvents were removed under reduced pressure to provide the title compound (0.346 g, 1.08 mmol, 97%) as a flocculent colorless powder; (Found: C, 59.8; H, 7.30; N, 12.7; $C_{16}H_{23}N_3O_4$ requires: C, 59.8; H, 7.21; N, 13.0%); R_F: 0.25 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.91 (1H, s (broad), NH), 8.20 (1H, s (broad), NH), 7.89 (2H, m, pyridyl-H), 7.68 (1H, app t, *J* = 8.3 Hz, pyridyl-H), 2.40 (4H, m, HO_2CCH_2C, $HO_2CCH_2CH_2CH_2CH_2$), 2.33 (2H, t, *J* = 7.5 Hz, $NHCOCH_2CH_2CH_2CH_3$), 1.95 (2H, dt, *J* = 7.1, 7.0 Hz, $HO_2CCH_2CH_2$), 1.75 (4H, m, $HO_2CCH_2CH_2CH_2$, $NHCOCH_2CH_2CH_2CH_3$), 1.63 (2H, m, $CH_2CH_2CH_3$), 0.89 (3H, t, *J* = 7.4 Hz, CH_3); ^{13}C NMR (75 MHz, MeOH-d_4) δ: 176.1, 173.7, 173.2, 150.5, 150.4, 140.0, 109.3, 36.7, 36.6, 33.5, 27.7, 25.0, 24.5, 22.3, 13.0 (1 signal not observed); ν_{max}/cm^{-1} (solid state): 3296, 2930, 1803, 1673, 1586; ESI-HRMS found m/z 322.1761 $[M + H]^+$ $C_{16}H_{23}N_3O_4$ requires 322.1767.

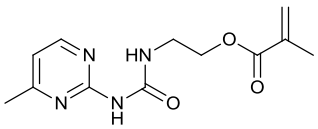
4-Vinylbenzyl 6-Oxo-6-(6-pentanamidopyridin-2-ylamino)hexanoate 13



To a stirring solution of 6-oxo-6-(6-pentamidopyridin-2-ylamino)hexanoic acid **11** (0.270 g, 0.840 mmol) in acetone (50 mL) was added potassium carbonate (0.116 g, 0.840 mmol), sodium iodide (10 mg, 0.07 mmol) and 18-crown-6 (5 mg, 0.006 mmol) and the reaction was then heated to reflux under nitrogen atmosphere. After 20 minutes 4-vinylbenzyl chloride **12** (0.14 mL, 0.95 mmol) was added dropwise over 5 minutes and the reaction was refluxed for a further 16 hr. The reaction mixture was concentrated under reduced pressure and the

remaining residue was purified using column chromatography (SiO_2, 60:40 hexane–EtOAc) followed by crystallization ($CHCl_3$ vs. hexane) to provide the title compound (0.213 g, 0.487 mmol, 58%) as a colourless flocculent solid; m.p: 98 – 101°C ($CHCl_3$ vs. hexane) (Found: C, 68.8; H, 6.85; N, 9.4; $C_{25}H_{31}N_3O_4$ requires: C, 68.6; H, 7.14; N, 9.6%); R_F: 0.29 (1:1 hexane–EtOAc);^{1}H NMR (400 MHz, MeOD-d_4) δ: 7.74 (2H, m, pyridyl-H), 7.68 (1H, app t, *J* = 7.9 Hz, pyridyl-H), 7.39 (2H, d, *J* = 6.4 Hz, ArH), 7.30 (2H, d, *J* = 6.4 Hz, ArH), 6.70 (1H, dd, *J* = 17.5, 10.8 Hz, $CH=CH_2$), 5.75 (1H, dd, *J* = 17.5, 0.9 Hz, CH=CHH' (cis)), 5.21 (1H, dd, *J* = 10.8, 0.9 Hz, CH=CHH' (trans)), 5.10 (2H, s, $ArCH_2O$), 2.44-2.38 (6H, m, $CH_2OC(O)CH_2$, $CH_2CH_2CH_2CH_3$, $CH_2O(O)CCH_2CH_2CH_2CH_2CO$), 1.73-1.64 (6H, m, $CH_2CH_2CH_2CH_3$, $CH_2O(O)CCH_2CH_2CH_2CH_2CO$), 1.41 (2H, app sext, *J* = 7.2 Hz, CH_2CH_3), 0.96 (3H, t, *J* = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, MeOD-d_4) δ:173.2, 171.6, 170.9, 149.4, 149.3, 140.9, 137.6, 136.3, 135.4, 128.5, 126.4, 114.4, 109.5, 109.4, 66.1, 37.6, 37.3, 33.9, 27.4, 24.7, 24.3, 22.3, 13.8; νmax/cm^{-1} (solid state): 3397, 3331, 2956, 2871, 1724, 1699, 1629, 1592, 1542, 1504; ESI-HRMS found m/z 438.2387 $[M + H]^+$ $C_{25}H_{32}N_3O_4$ requires 438.2393.

2-(3-(4-Methylpyrimidin-2-yl)ureido)ethyl methacrylate 3



A solution of 4-methyl-2-aminopyrimidine **4** (0.580 g, 5.30 mmol) in THF (12 mL) was stirred at reflux under nitrogen atmosphere for 3 hr. 2-Isocyanatoethyl methacrylate **5** (0.93 mL, 6.6 mmol) was then added dropwise to the reaction mixture over 10 minutes. The reaction was stirred at reflux for a further 20 hr. The reaction mixture was allowed to cool to room temperature, poured onto H_2O (50 mL) and extracted with EtOAc (3 × 50 mL). The organic portions were collected and washed with H_2O (3 × 50 mL). The organics were collected and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified via column chromatography (SiO_2, gradient of 100:0 – 50:50

CH_2Cl_2–EtOAc) followed by recrystallization (1:1 acetonitrile–MeOH vs. H_2O) to provide the title compound (0.42 g, 1.59 mmol, 30%) as a flocculent colourless powder; m.p: 63 – 65°C (acetonitrile–MeOH vs. H_2O) (Found C, 54.6; H, 6.10; N, 21.3; $C_{12}H_{16}N_4O_3$ requires C, 54.5; H; 6.10; N, 21.2%); R_F: 0.50 (EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.36 (1H, s, pyrimidyl-NHCO), 8.30 (1H, d, *J* = 5.1 Hz, pyrimidyl-H), 7.59 (1H, s, pyrimidyl-NHCONH), 6.75 (1H, d, *J* = 5.1 Hz, pyrimidyl-H), 6.16 (1H, s, CHH'=CCH3(cis)), 5.59 (1H, s, CHH'=CCH3(trans)), 4.33 (2H, t, *J* = 5.4 Hz, NHCH2CH2O), 3.70 (2H, t, *J* = 5.7 Hz, $NHCH_2CH_2O$), 2.43 (3H, s, CH_3-pyrimidyl, 1.95 (3H, s, HH'C=CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.3, 167.1, 157.9, 157.3, 154.7, 136.1, 125.8, 114.2, 63.8, 38.9, 24.1, 18.3; νmax/cm^{-1} (solid state): 3217, 2974, 1891, 1717, 1682, 1600, 1547; ESI-HRMS m/z found 265.1295 $[M + H]^+$ $C_{12}H_{17}N_4O_3$ requires 265.1301.

Procedure for PS–co–PS-DAP Polymerization

The required amounts of styrene, S-DP co-monomer (if required) and cyanomethyl dodecyl trithiocarbonate were transferred to an ampoule with stirrer bar under nitrogen atmosphere. The reaction mixture was thoroughly degassed by purging with nitrogen for 20 min, followed by three freeze-pump-thaw cycles. The reaction mixture was placed into a preheated oil bath at 110°C and stirred for 16.5 hr. After this time, the flask was immediately cooled to 0°C to prevent any further polymerization. Precipitation (minimum amount of THF vs. a 100-fold excess of MeOH at 0°C) twice, followed by removal of residual solvent under reduced pressure provided the title material as a flocculent colorless solid.

PS Standard 16

General procedure for PS-co-S-DP polymerisation was followed adding styrene (1.0 mL, 8.7 mmol) and cyanomethyl dodecyl trithiocarbonate (3.1 mg, 0.01 mmol). Yield: 0.60 g, 60%; M_n (g mol^{-1}): 22,000 (GPC); PDI: 1.26 (GPC); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.20 – 6.20

(polymer Ar-H), 2.25 – 1.60 (polymer CH-Ar), 1.60 – 1.20 (polymer CH_2CH-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 145.2, 128.0 – 127.6 (m), 125.7, 40.4.

PS–co–PS-DAP 17

General procedure for PS-co-S-DP polymerization was followed adding styrene (1.0 mL, 8.7 mmol) and cyanomethyl dodecyl trithiocarbonate (3.2 mg, 0.01 mmol), to a schlenk tube containing co-monomer S-DP (30.8 mg, 0.07 mmol). Yield: 0.31 g, 30%; M_n (g mol^{-1}): 22,400 (GPC); Đ: 1.35 (GPC); ^1H NMR (300 MHz, $CDCl_3$) δ: 7.85 (2H, m, pyridyl-H), 7.62 (1H, m, pyridyl-H), 7.20 – 6.20 (polymer Ar-H), 5.03 (2H, m, Ar-$CH_2OC(O)$), 2.25 – 1.60 (polymer CH-Ar), 1.60 – 1.20 (polymer CH_2CH-Ar); 0.88 (3H, t, J = 6.5 Hz, $CH_2CH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 145.4, 128.3 – 127.0 (m), 125.7 – 125.5 (m), 40.3.

PS–co–PS-DAP 18

General procedure for PS-co-S-DP polymerization was followed adding styrene (0.5 mL, 4.4 mmol) and cyanomethyl dodecyl trithiocarbonate (1.6 mg, 0.005 mmol), to a schlenk tube containing co-monomer S-DP (59.0 mg, 0.134 mmol). Yield: 0.42 g, 75%; M_n (g mol^{-1}): 21,000 (GPC); Đ: 1.24 (GPC); ^1H NMR (300 MHz, $CDCl_3$) δ: 7.85 (2H, m, pyridyl-H), 7.62 (1H, m, pyridyl-H), 7.20 – 6.20 (polymer Ar-H), 5.03 (2H, m, Ar-$CH_2OC(O)$), 2.25 – 1.60 (polymer CH-Ar), 1.60 – 1.20 (polymer CH_2CH-Ar); 0.88 (3H, t, J = 6.5 Hz, $CH_2CH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): 145.7 – 145.1 (m), 128.0 – 12.5 (m), 125.7, 40.4.

PS–co–PS-DAP 19

General procedure for PS-co-S-DP polymerization was followed adding styrene (0.5 mL, 4.4 mmol) and cyanomethyl dodecyl trithiocarbonate (1.7 mg, 0.005 mmol), to a schlenk tube containing co-monomer S-DP (121 mg, 0.268 mmol). Yield: 0.37 g, 60%; M_n (g mol^{-1}): 21,600 (GPC); Đ: 1.30 (GPC); ^1H NMR (300 MHz, $CDCl_3$) δ: 7.85 (2H, m, pyridyl-H), 7.62 (1H, m, pyridyl-H), 7.20 – 6.20 (polymer Ar-H), 5.03 (2H, m, Ar-$CH_2OC(O)$), 2.25 – 1.60 (polymer CH-Ar), 1.60 – 1.20 (polymer CH_2CH-Ar); 0.88 (3H, t, J = 6.5 Hz, $CH_2CH_2CH_3$);

^{13}C NMR (75 MHz, $CDCl_3$) δ: 145.3, 140.9, 128.0 – 127.7 (m), 126.8 – 125.5 (m), 109.4, 40.3, 37.2, 33.9, 27.4, 24.7, 24.3, 22.4, 13.9.

Procedure for PMMA–co–PMMA-UP Polymerization

The required amount of MMA-UP co-monomer (if required) was transferred to an ampoule with stirrer bar under nitrogen atmosphere. A 5 mL stock solution of 4-cyano-4-((dodecylsulfanylthiocarbonyl)sulfanyl)pentanoic acid and azobutyronitrile (AIBN) dissolved in methyl methacrylate monomer was also prepared, and the required aliquot of stock solution was added to the ampoule by syringe addition. The reaction mixture was thoroughly degassed by purging with nitrogen for 20 min, followed by three freeze-pump-thaw cycles. The reaction mixture was placed into a preheated oil bath at 90 °C and stirred for 3 hr. After this time, the flask was immediately cooled to 0 °C to prevent any further polymerization. Precipitation (minimum amount of THF vs. 100-fold excess of petroleum ether at 0°C) twice, followed by removal of residual solvent under reduced pressure provided the title material as a flocculent colorless powder.

PMMA Standard 23

General Procedure for PMMA-co-MMA-UP polymerization was followed adding methyl methacrylate (1.0 mL, 9.39 mmol), 4-cyano-4-((dodecylsulfanylthiocarbonyl)sulfanyl) pentanoic acid (21.8 mg, 0.078 mmol) and AIBN (0.52 mg, 0.0032 mmol). Yield: 0.612 g, 60%; M_n (g mol^{-1}): 13,600 (GPC); Đ: 1.13 (GPC); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.66 (polymer CH_3O), 2.10 – 1.70 (polymer CH_2), 1.60 – 0.80 (polymer CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 178.1, 177.8, 177.0, 54.4, 51.8, 44.9, 44.5, 29.1, 22.6, 19.4, 18.7, 16.4.

PMMA–co–PMMA-UP 24

General Procedure for PMMA-co-MMA-UP polymerization was followed adding methyl methacrylate (1.0 mL, 9.39 mmol), 4-cyano-4-((dodecylsulfanylthiocarbonyl)sulfanyl) pentanoic acid (22.5 mg, 0.080 mmol) and AIBN (0.56 mg, 0.0034 mmol) to a schlenk tube

containing co-monomer MMA-UP (76.7 mg, 0.290 mmol). Yield: 0.324 g, 30%; M_n (g mol^{-1}): 10,200 (GPC); Đ: 1.24 (GPC); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.30 – 9.45 (1H, br s, $NHCH_2$), 8.53 (1H, br s, pyrimidyl-H), 6.85 (1H, br s, pyrimidyl-H), 4.15 (2H, br s, CH_2OC), 3.66 (polymer CH_3O, co-monomer CH_2CH_2OC), 2.50 (3H, br s, CH_3-pyrimidyl), 2.10 – 1.70 (polymer CH_2), 1.60 – 0.80 (polymer CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 178.1, 177.8, 177.0, 54.4, 52.6, 51.8, 44.9, 44.5, 29.6, 24.2, 22.7, 18.7, 16.4.

PMMA–co–PMMA-UP 25

General Procedure for PMMA-co-MMA-UP polymerization was followed adding methyl methacrylate (0.5 mL, 4.7 mmol), 4-cyano-4-((dodecylsulfanylthiocarbonyl)sulfanyl) pentanoic acid (11.6 mg, 0.040 mmol) and AIBN (0.31 mg, 0.0019 mmol) to a schlenk tube containing co-monomer MMA-UP (79.2 mg, 0.300 mmol). Yield: 0.180 g, 25%; M_n (g mol^{-1}): 10,400 (GPC); Đ: 1.26 (GPC); ^{1}H NMR (300 MHz, $CDCl_3$): 9.30 – 9.45 (1H, br s, $NHCH_2$), 8.53 (1H, br s, pyrimidyl-H), 6.85 (1H, br s, pyrimidyl-H), 4.15 (2H, br s, CH_2OC), 3.66 (polymer CH_3O, co-monomer CH_2CH_2OC), 2.50 (3H, br s, CH_3-pyrimidyl), 2.10 – 1.70 (polymer CH_2), 1.60 – 0.80 (polymer CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): 178.1, 177.8, 177.0, 54.4, 51.8, 44.9, 44.5, 22.6, 18.7, 16.4.

PMMA–co–PMMA-UP 26

General Procedure for PMMA-co-MMA-UP polymerization was followed adding methyl methacrylate (1.0 mL, 9.39 mmol), 4-cyano-4-((dodecylsulfanylthiocarbonyl)sulfanyl) pentanoic acid (24.8 mg, 0.082 mmol) and AIBN (0.69 mg, 0.0042 mmol) to a schlenk tube containing co-monomer MMA-UP (338 mg, 1.28 mmol). Yield: 0.945 g, 90%; M_n (g mol^{-1}): 15,100 (GPC); Đ: 1.32 (GPC); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.30 – 9.45 (1H, br s, $NHCH_2$), 8.53 (1H, br s, pyrimidyl-H), 6.85 (1H, br s, pyrimidyl-H), 4.15 (2H, br s, CH_2OC), 3.66 (polymer CH_3O, co-monomer CH_2CH_2OC), 2.50 (3H, br s, CH_3-pyrimidyl), 2.10 – 1.70

(polymer CH_2), 1.60 – 0.80 (polymer CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 178.1, 177.8, 176.9, 68.0, 54.4, 51.8, 44.8, 44.5, 22.6, 18.7, 16.4.

Dibenzyl carbonotrithioate[1]

To a solution of K_3PO_4 (1.72 g, 8.09 mmol) in acetone (20 mL) was added benzyl mercaptan (1.00 g, 7.35 mmol). The reaction mixture was stirred at room temperature for 10 minutes before adding carbon disulfide (1.68 g, 22.1 mmol) and stirring for a further 10 minutes under a nitrogen atmosphere. Benzyl bromide was then added to the reaction mixture whereby a precipitate was immediately observed. The reaction was stirred for a further 5 minutes before filtering the precipitate and washing with a further portion of acetone (50 mL). The filtrate was concentrated under reduced pressure and the remaining residue purified via column chromatography (SiO_2, hexane) followed by crystallisation (MeOH) to provide the title compound (1.96 g, 6.76 mmol, 92%) as a bright yellow, odorous powder; m.p: 27 – 29°C ($CHCl_3$); R_F: 0.20 (hexane); ^1H NMR (300 MHz, $CDCl_3$) δ: 7.38 – 7.25 (10H, m, ArH), 4.65 (4H, s, CH_2). Data in accordance with those reported in the literature.

Synthesis of 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid[1]

To a solution of K_3PO_4 (1.02 g, 6.59 mmol) in acetone (30 mL) was added dodecane thiol (1.34 g, 6.59 mmol). The reaction mixture was stirred at room temperature for 10 minutes before adding carbon disulfide (1.37 g, 18.0 mmol) and stirring for a further 10 minutes under a nitrogen atmosphere. 2-bromoisobutyric acid (1.00 g, 6.00 mmol) was then added to the reaction mixture whereby a precipitate was immediately observed. The reaction was stirred for a further 5 minutes before filtering the precipitate and washing with a further portion of acetone (50 mL). The filtrate was concentrated under reduced pressure and the remaining residue purified via column chromatography (SiO_2, CH_2Cl_2) followed by crystallization (MeOH) to provide the title compound (1.80 g, 4.90 mmol, 82%) as a bright yellow, odorous powder; m.p: 40 – 41°C (MeOH); ^1H NMR (400 MHz, $CDCl_3$) δ: 11.19 (1H, br s, COOH),

3.20 (2H, t, J = 7.6 Hz, $(CH_2)_{10}CH_2S$), 1.73 (6H, s, $C(CH_3)_2$), 1.71 – 1.64 (2H, m, $(CH_2)_9CH_2CH_2S$), 1.40 – 1.24 (18H, m, $CH_3(CH_2)_9$), 0.88 (3H, t, J = 7.2 Hz, CH_3). Data in accordance with those reported in the literature.

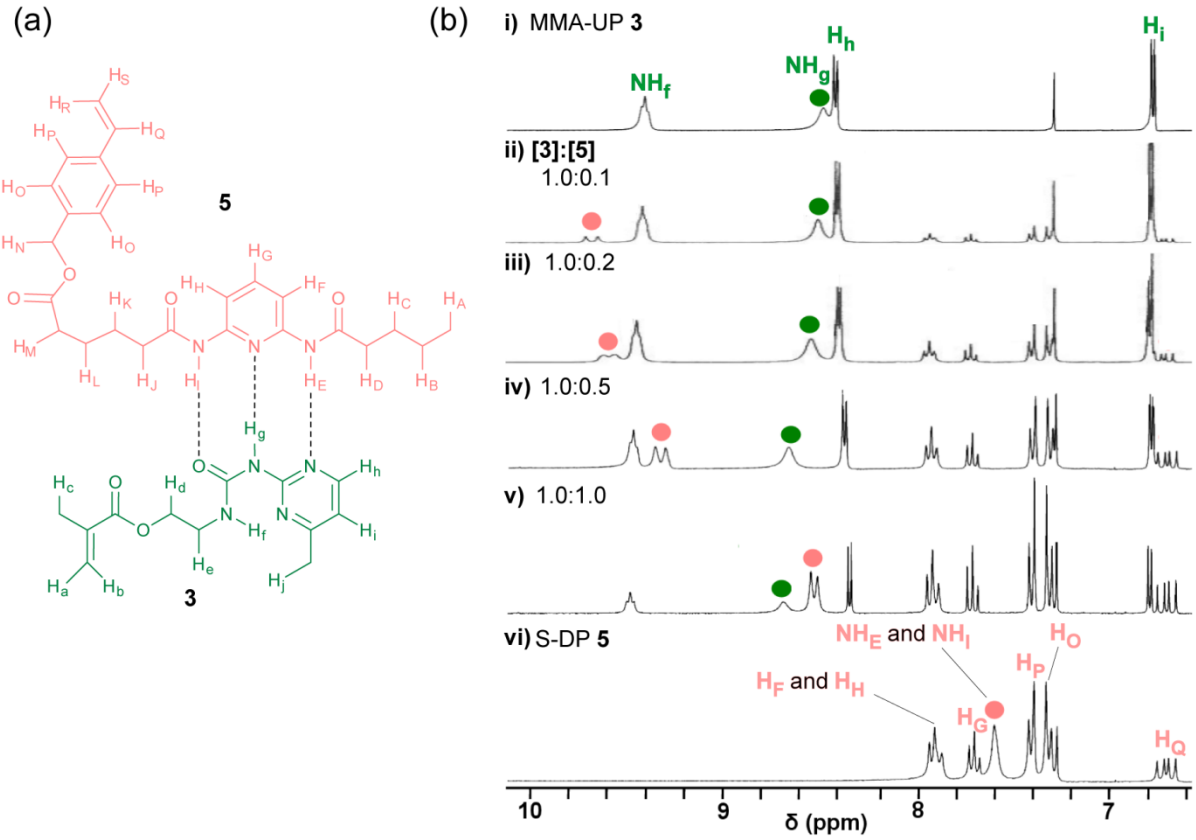


Figure ESI 1 ^{1}H NMR stack plot ($CDCl_3$, 300 MHz) of comonomer components. (a) MMA-UP **3** (20 mM) alone; (b – e) Mixtures of **5** and **3** at the stoichiometries shown (concentrations relative to 20 mM MMA-UP **3**); (f) S-DP **5** (20 mM) alone. Key shifts in proton resonances are highlighted in pink and green for **3** and **5** repectively.

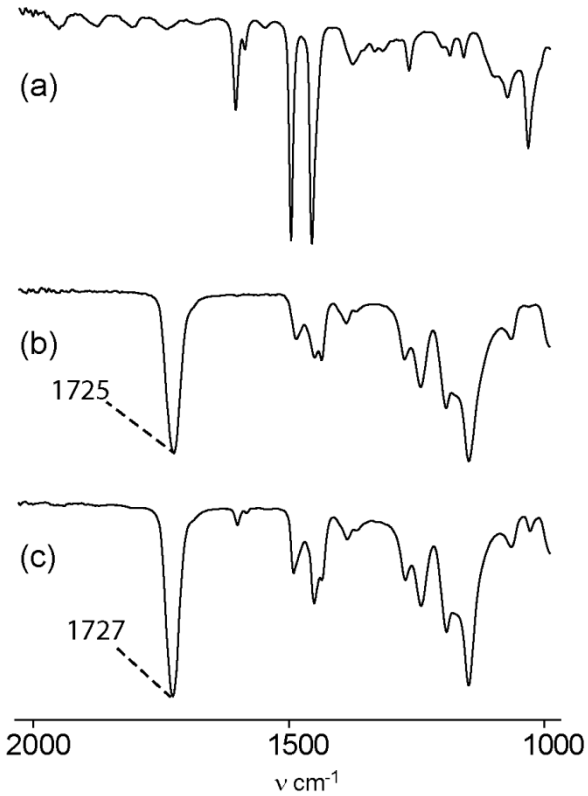


Figure ESI 2 IR analysis of polymer blends obtained from drop casting a solution (10 mg/ml $CDCl_3$) of PS **16** and PMMA **23** (a) PS **16**; (b) PMMA **23**; (c) PS **16** and PMMA **23**.

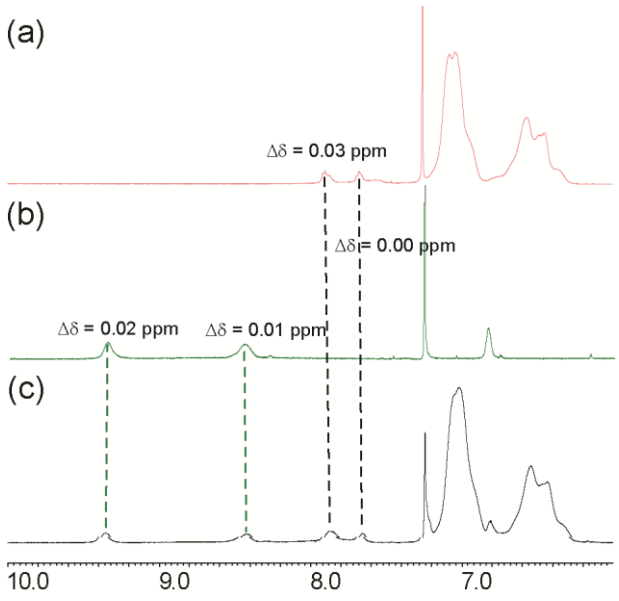


Figure ESI 3 ^{1}H NMR analysis (500 MHz, 10 mg/ml $CDCl_3$) of polymer blends of PS–*co*–PS-DAP **19** and PMMA–*co*–PMMA-UP **26** (a) PS–*co*–PS-DAP **19**; (b) PMMA–*co*–PMMA-UP **26**; (c) PS–*co*–PS-DAP **19** and PMMA–*co*–PMMA-UP **26**.

Gel-Permeation Chromatography (GPC) Traces

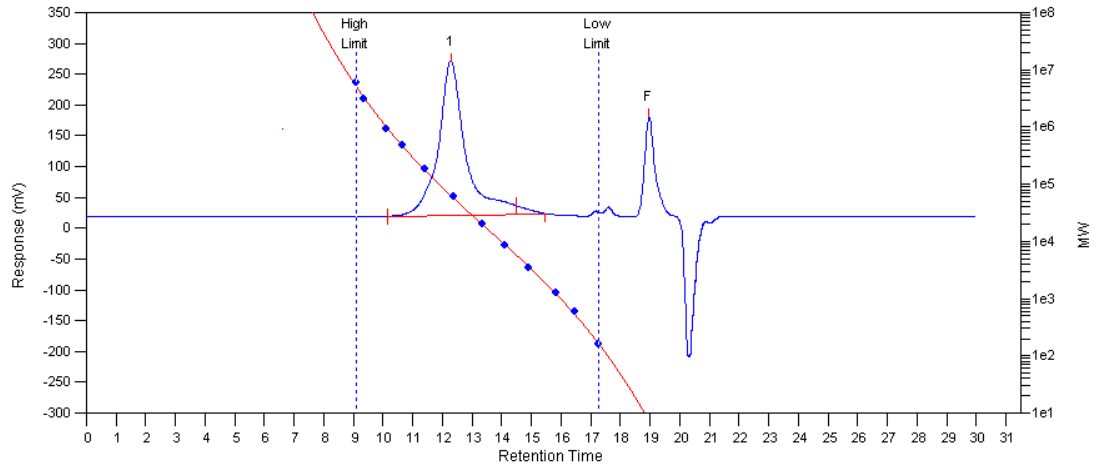


Figure ESI 4 Gel-permeation chromatography trace of PS **16**.

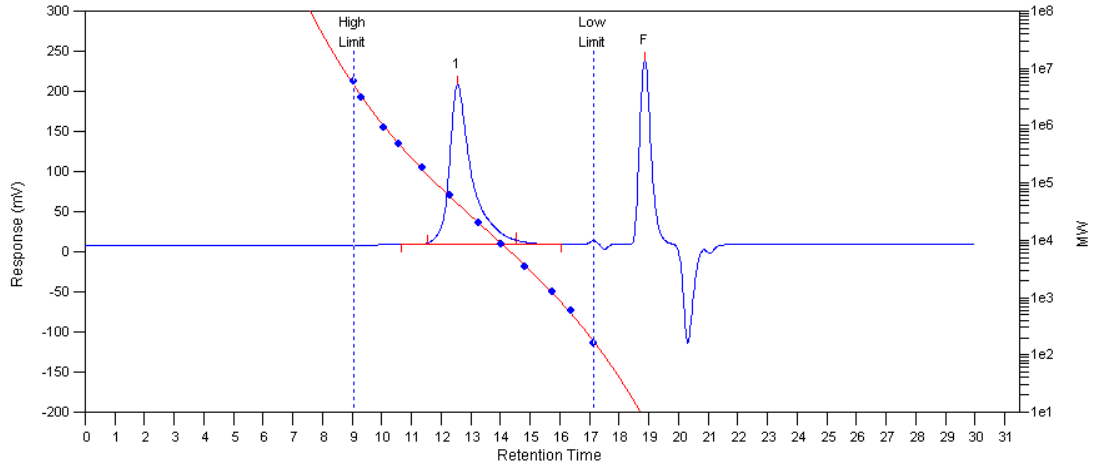


Figure ESI 5 Gel-permeation chromatography trace of PS–*co*–PS-DP **17**.

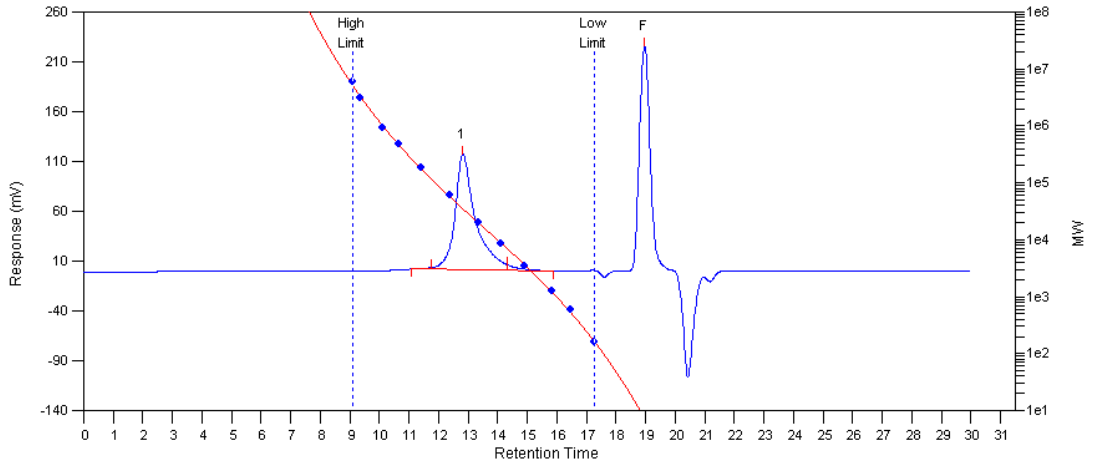


Figure ESI 6 Gel-permeation chromatography trace of PS–*co*–PS-DP **18**.

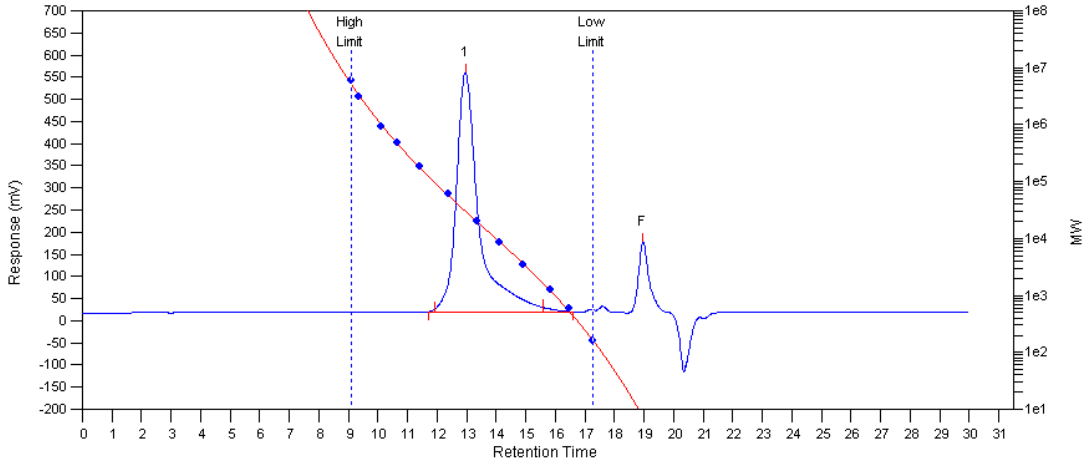


Figure ESI 7 Gel-permeation chromatography trace of PS–*co*–PS-DP **19**.

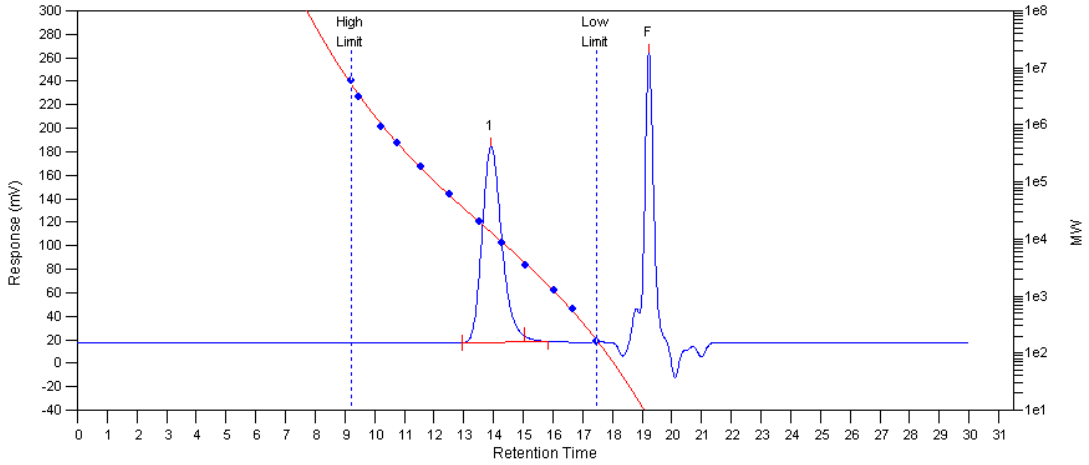


Figure ESI 8 Gel-permeation chromatography trace of PMMA **23**.

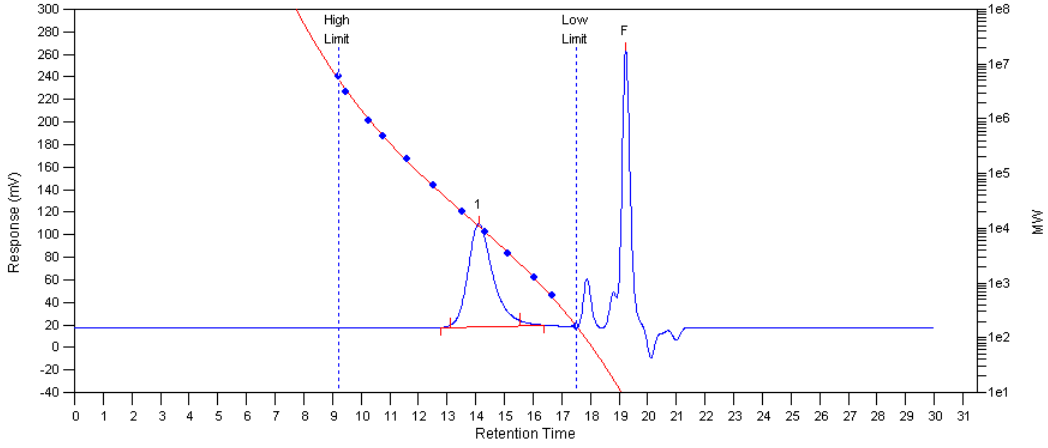


Figure ESI 9 Gel-permeation chromatography trace of PMMA–*co*–MMA-UP **24**.

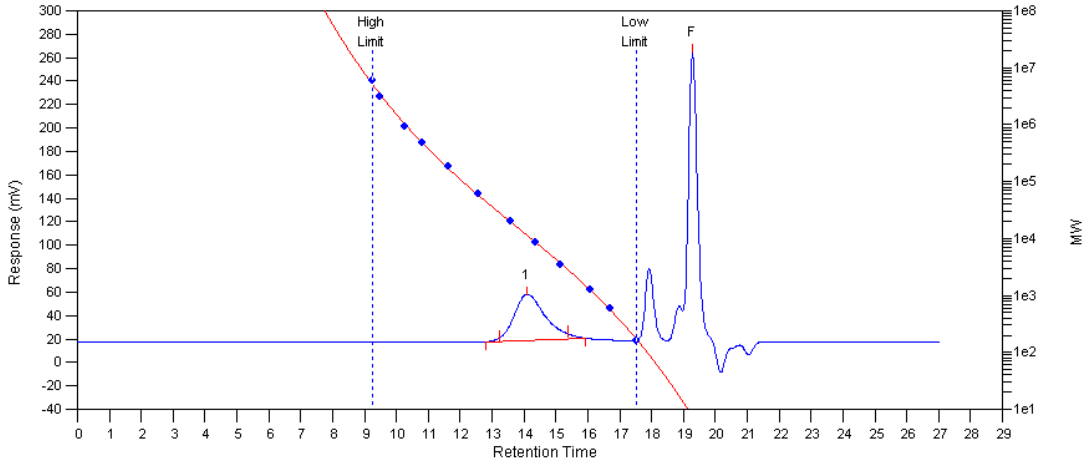


Figure ESI 10 Gel-permeation chromatography trace of PMMA–*co*–MMA-UP **25**.

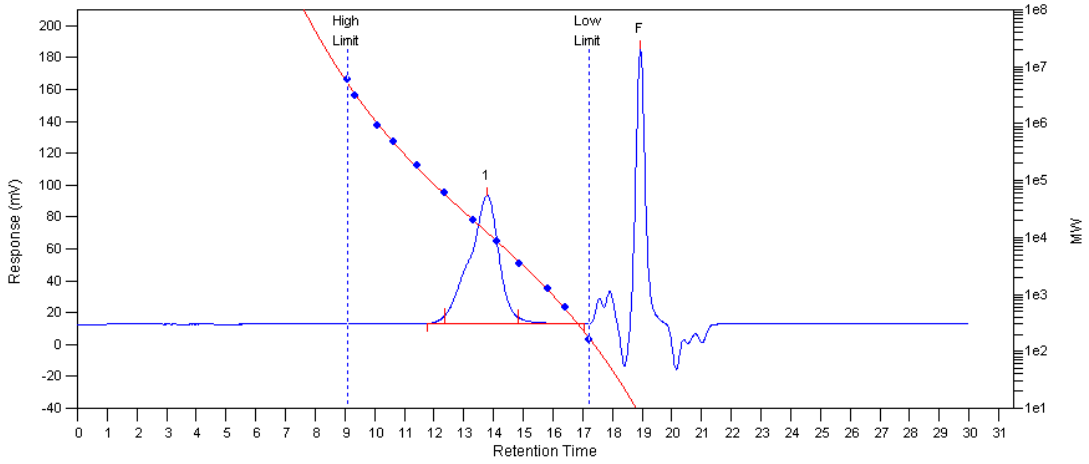


Figure ESI 11 Gel-permeation chromatography trace of PMMA–*co*–MMA-UP **26**.

NMR Spectra of Polymers

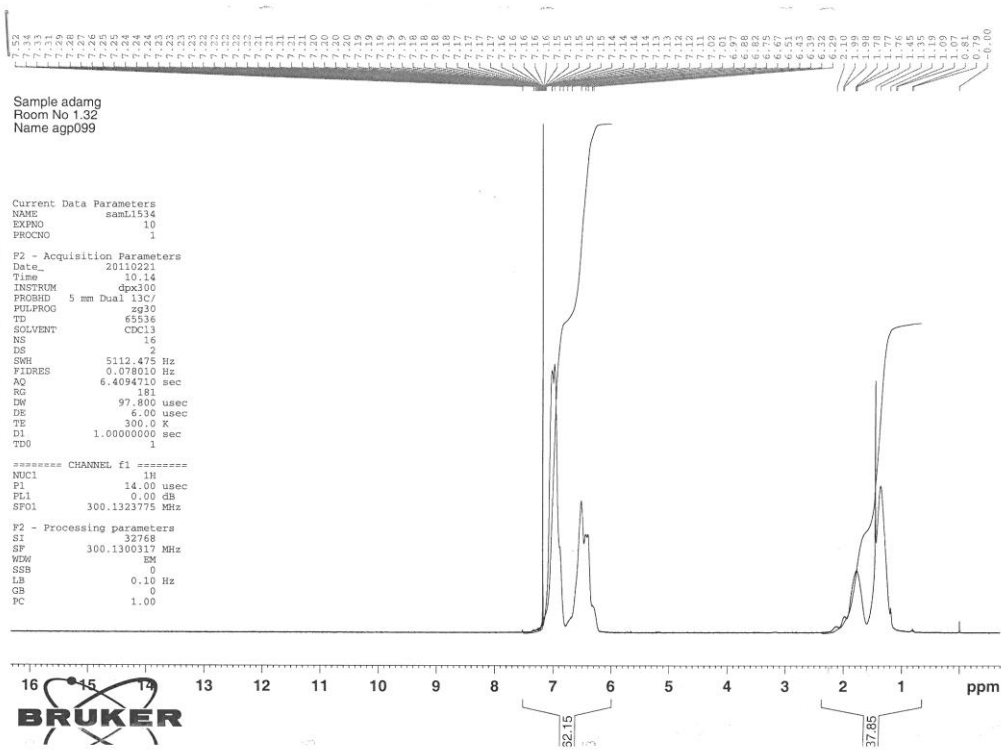


Figure ESI 12 NMR spectrum of PS **16**.

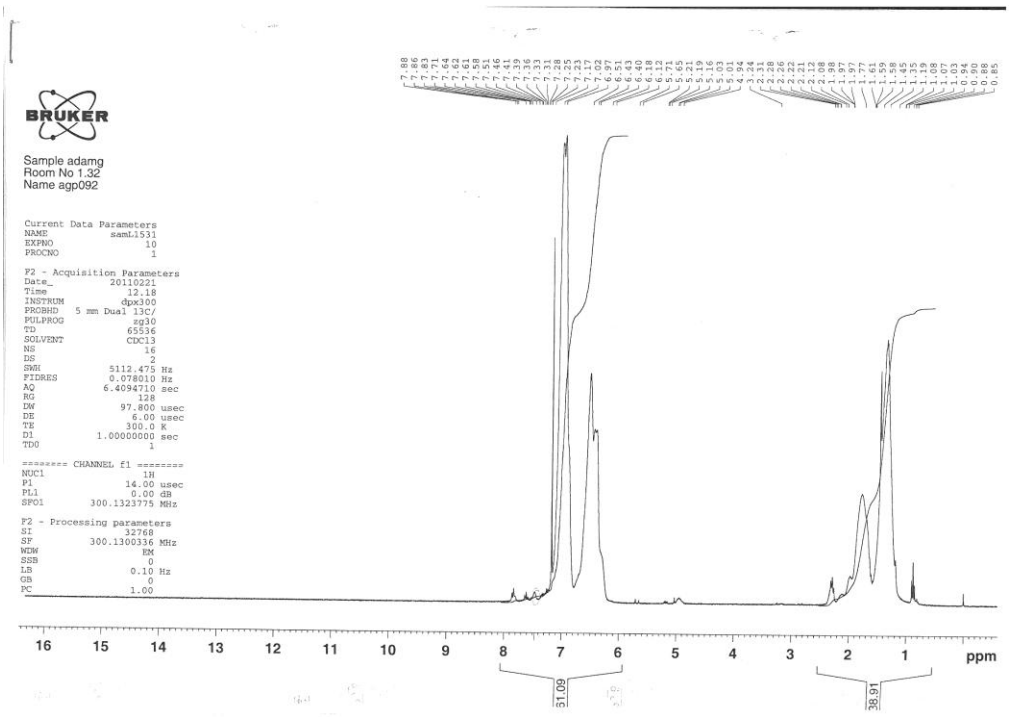


Figure ESI 13 NMR spectrum of PS–*co*–PS-DP **17**.

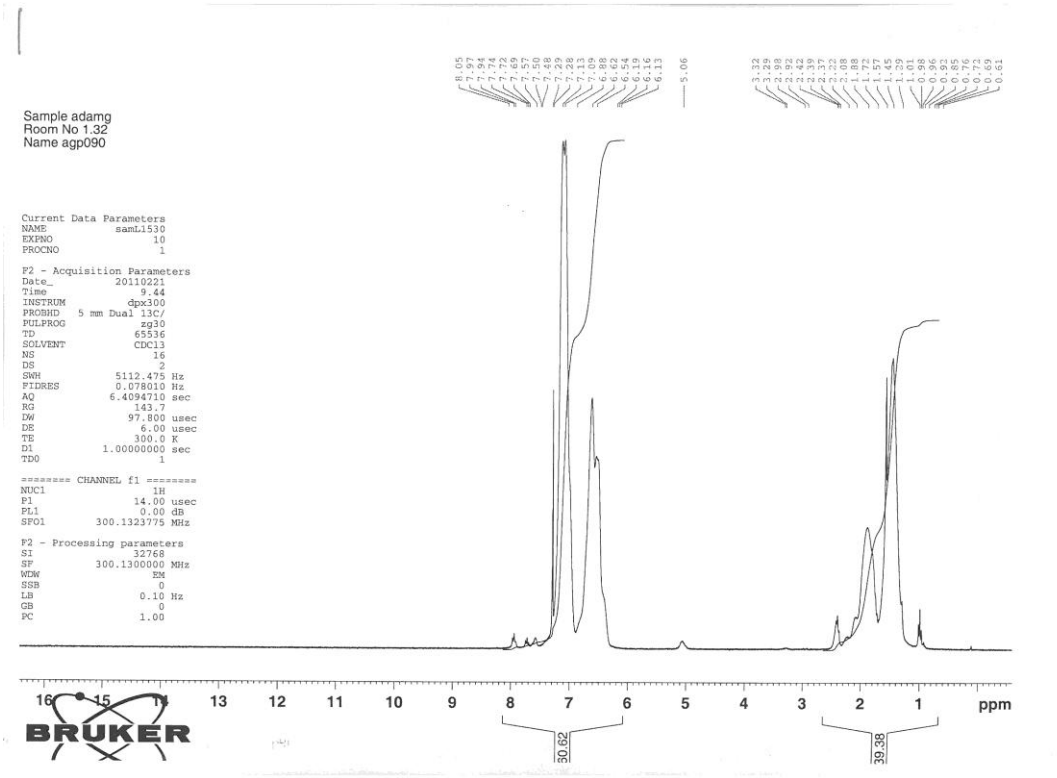


Figure ESI 14 NMR spectrum of PS–*co*–PS-DP **18**.

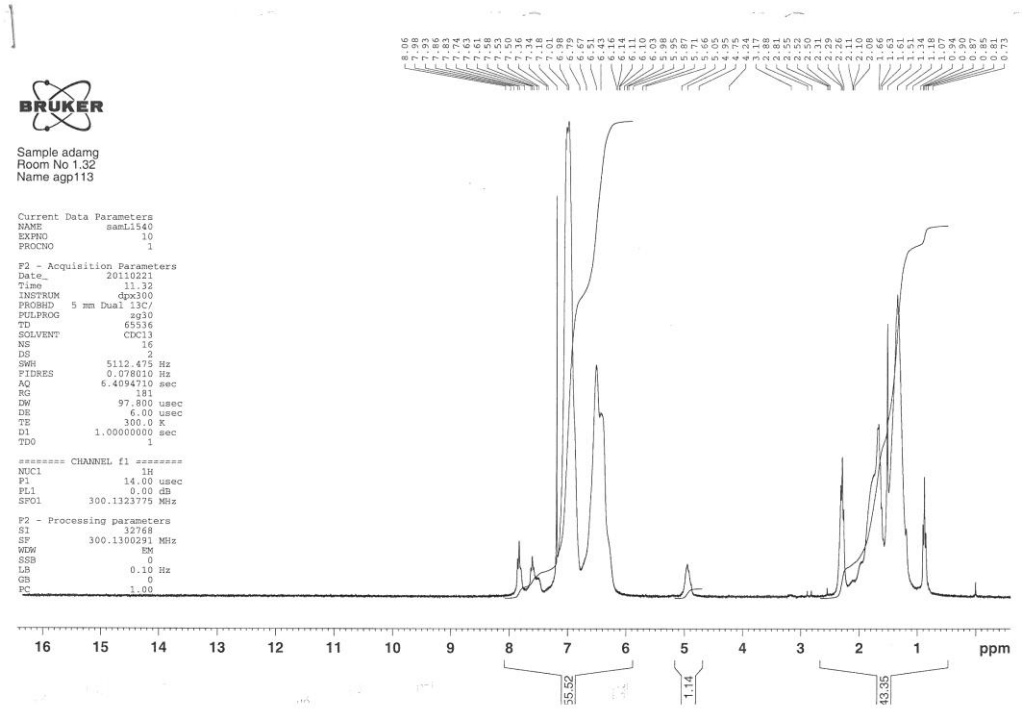


Figure ESI 15 NMR spectrum of PS–*co*–PS-DP **19**.

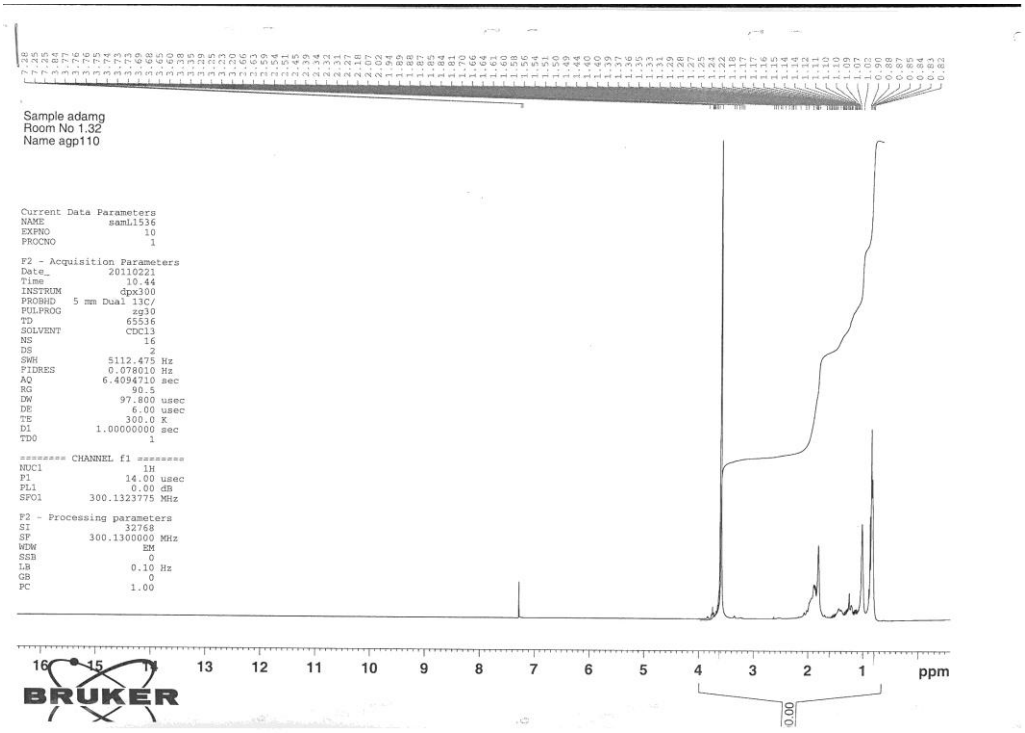


Figure ESI 16 NMR spectrum of PMMA **23**.

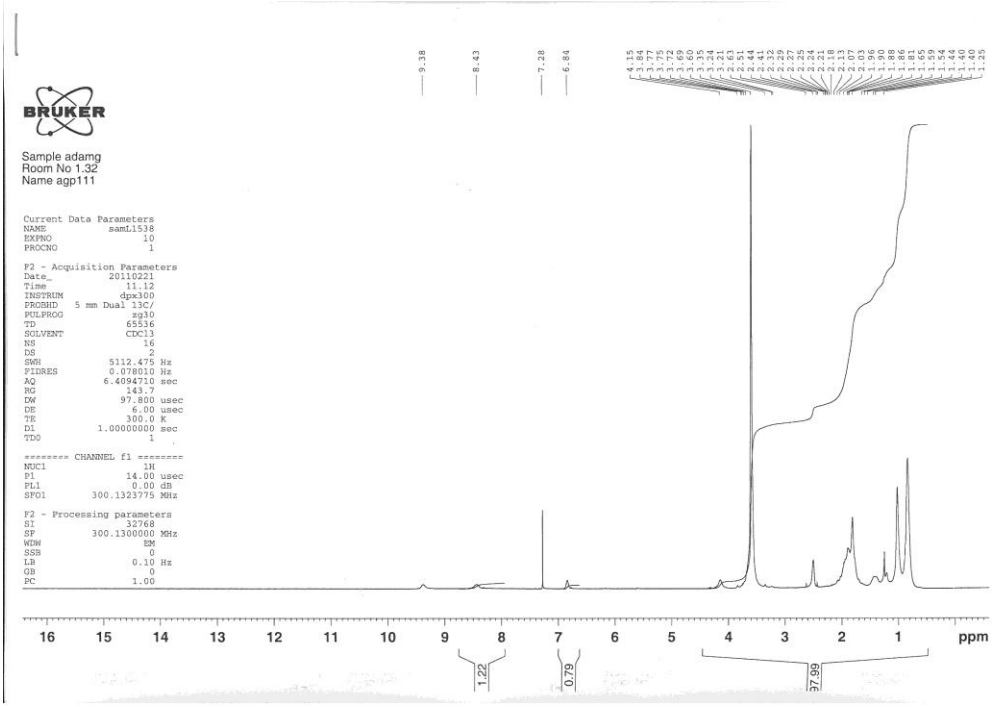


Figure ESI 17 NMR spectrum of PMMA–*co*–MMA-UP **24**.

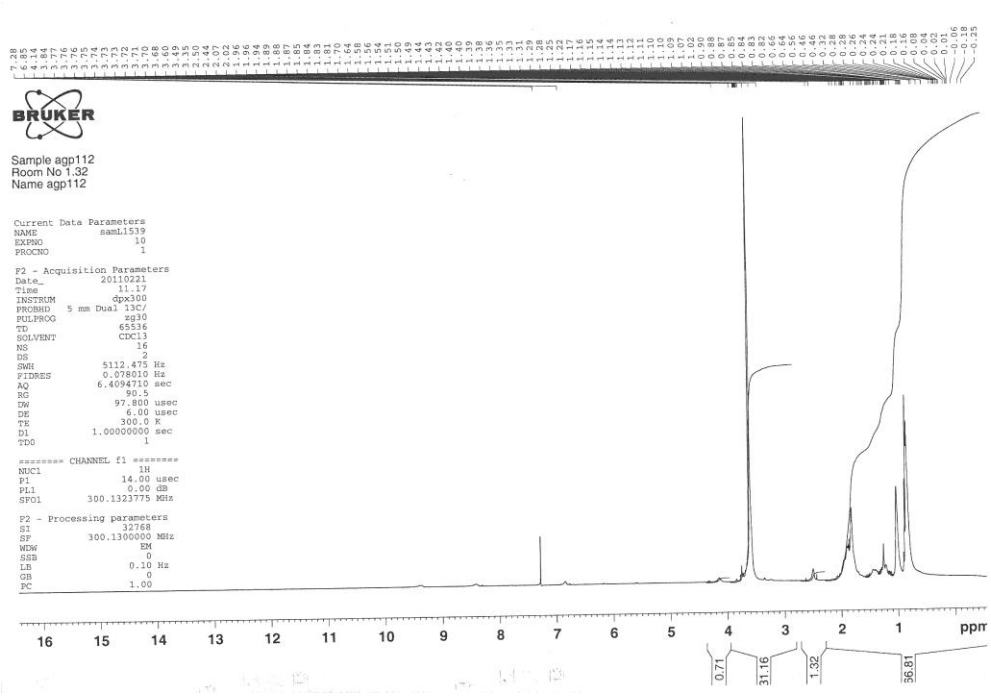


Figure ESI 18 NMR spectrum of PMMA–*co*–MMA-UP **25**.

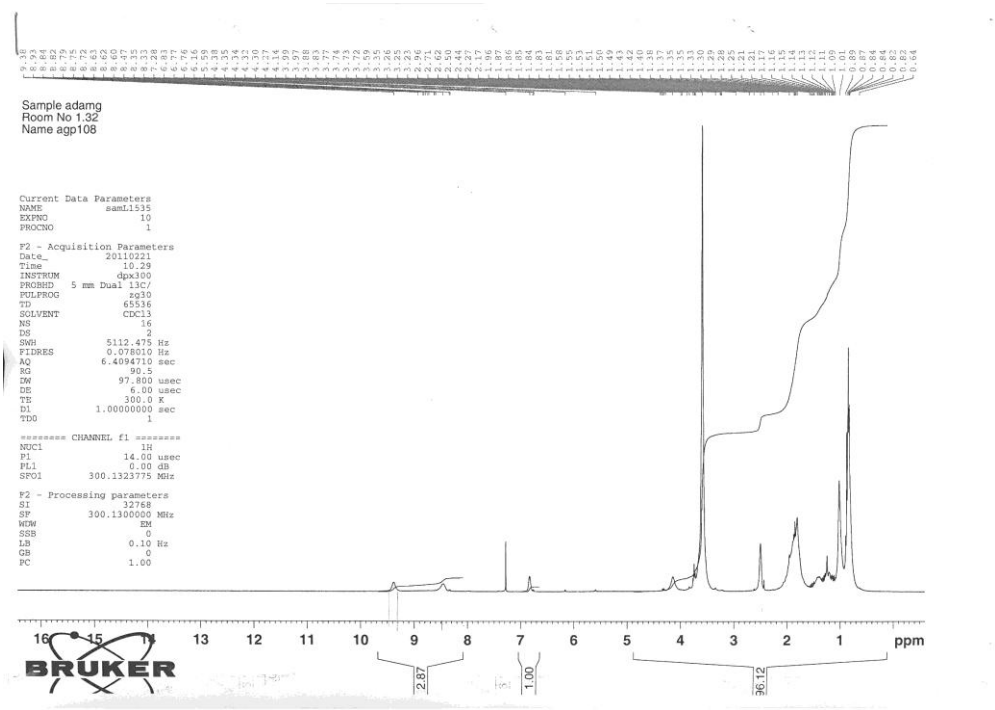


Figure ESI 19 NMR spectrum of PMMA–*co*–MMA-UP **26**.

(1) Skey, J.; O'Reilly, R. K. *Chem. Commun.* **2008**, 4183.