Supplementary Material (ESI) for Chemical Communications

Electronic supplementary information

Facile one pot synthesis of a range of reversible addition fragmentation chain transfer (RAFT) agents

*Jared Skey and Rachel K. O'Reilly**

Methods

^{1}H NMR and ^{13}C NMR collected on a Bruker DPX-400 or 500 spectrometer using $CDCl_3$. Chemical shifts are reported in ppm (δ) relative to $CHCl_3$ (7.26 ppm for ^{1}H and 77.2 ppm for ^{13}C) or CH_3OD (3.31 ppm for ^{1}H and 49.1 ppm for ^{13}C) as internal reference. GPC data for all polymers were obtained in THF (Shimadzu UFLC autosampler with Polymer Laboratories gel 5 μm Mixed C column) or $CHCl_3$ (Viscotek VE1122 solvent delivery system two GMHHRH-H viscotek columns and GMHHRH-H guard column) at room temperature with PMMA standards at a flow rate of 1 $mlmin^{-1}$. All infrared spectra were collected on a Perkin Elmer Spectrum 100 FTIR ATR unit. Mass spectra were recorded on a Waters 2795 LC with an Atlantis dC18 3μ column eluting a H_2O/Acetonitrile gradient and a Waters Micromass ZQ mass analyzer.

Materials

AIBN (2,2'-Azobis(2-methylpropionitrile)) was recrystallized twice from methanol and stored in the dark at 4 °C. *Tert*-butyl acrylate (^{t}BuA), Styrene (S), *4*-vinyl benzyl

chloride, methyl methacrylate (MMA) and vinyl acetate (VAc) were purified by vacuum distillation from CaH_2 and then stored at –4 °C. All other materials were used as received from Sigma-Aldrich Company. 2,2,5-Trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane and *tert*-butyl-O-(1-(4-(chloromethyl)phenyl)ethyl)-*N*-(2-methyl-1-phenylpropyl)hydroxylamine were synthesized according to literature methods.[1]

Compound (**1**), dibenzyl carbonotrithioate, was prepared by adding benzyl mercaptan (1.00 g, 7.35 mmol) to a stirred suspension of K_3PO_4 (1.72 g, 8.09 mmol) in acetone (20 ml) and stirring for ten minutes. CS_2 (1.68 g, 22.06 mmol) was added and the solution turned bright yellow. After stirring for ten minutes benzyl bromide (1.26 g, 7.35 mmol) was added and an instant precipitation of KBr was noted. After stirring for five minutes the suspension was filtered and the cake was washed with acetone (2 x 20 ml). After removing the solvent from the filtrate under reduced pressure the resulting yellow residue was purified by column chromatography on silica using a petroleum ether/ethyl acetate gradient to yield a bright yellow oil **1** (96 %) that crystallized on refrigeration. Found C, 62.14; H, 4.88; $C_{15}H_{14}S_3$ requires C, 62.02; H, 4.86; ν_{max}/cm^{-1} 3062, 3027, 2899, 1493, 1452, 1392, 1233, 1057, 793, 760, 680. δ_H (400 MHz, $CDCl_3$) = 7.38-7.25 (10H, m, Ph), 4.65 (4H, s, 2CH_2); δ_C (400 MHz, $CDCl_3$) = 223.2, 135.4, 129.7, 129.2, 128.2, 42.0; *m*/*z* (EI) 291, 290, 181, 132.

Compound (**1a**), dibenzyl carbonotrithioate, was prepared by adding benzyl mercaptan (1.00 g, 7.35 mmol) to a stirred suspension of K_3PO_4 (1.72 g, 8.09 mmol) in acetone (20 ml) and stirring for ten minutes. CS_2 (1.68 g, 22.06 mmol) was added

and the solution turned bright yellow. After stirring for ten minutes benzyl bromide (1.26 g, 7.35 mmol) was added and an instant precipitation of KBr was noted. After stirring for five minutes the suspension was filtered and the cake was washed with acetone (2 x 20 ml). After removing the solvent from the filtrate under reduced pressure a bright yellow oil **1a** (97 %) crystallized on refrigeration and was found to have identical characterisation data as for compound (**1**).

Compound (**2**), 3-(benzylthiocarbonothioylthio)propanoic acid, was prepared in an analogous manner to that of compound (**1**) using 1-mercapto propionic acid (1.00 g, 9.43 mmol), K_3PO_4 (2.00 g, 9.43 mmol), CS_2 (2.15 g, 28.30 mmol) and benzyl bromide (1.61 g, 9.43 mmol). After stirring for ten minutes the solvent was removed under reduced pressure and the residue was added to a saturated solution of brine (100 ml) and extracted with CH_2Cl_2 (2 x 100 ml) and washed with saturated brine solution (3 x 100 ml). After drying the organic extracts over $MgSO_4$ the solvent was removed under reduced pressure to yield a canary yellow crystalline solid **2** (> 99 %). Found C, 48.71; H, 4.43; $C_{11}H_{12}O_2S_3$ required C, 48.50; H, 4.44; ν_{max}/cm^{-1} 3000-2500 (broad), 2915, 2587, 1697, 1405, 1270, 1204, 1068, 838, 798, 669; δ_H (400 MHz, $CDCl_3$) = 10.05-9.50 (1H, br s, COO*H*), 7.14-7.32 (5H, m, Ph), 4.52 (2H, s, C*H*$_2$-Ph), 3.59 (2H, t, S-C*H*$_2$-CH$_2$), 2.75 (2H, t, S-CH$_2$-C*H*$_2$); δ_C (400 MHz, $CDCl_3$) = 223.2, 177.9, 135.2, 129.7, 129.1, 128.3, 42.0, 33.4, 31.3; *m*/*z* (EI) 273, 179.

Compound (**3**), benzyl 2-hydroxyethyl carbonotrithioate, was prepared in an analogous manner to compound (**1**) using 2-mercapto ethanol (1.00 g, 12.82 mmol), K_3PO_4 (2.71 g, 12.82 mmol), CS_2 (2.92 g, 38.46 mmol) and benzyl bromide (2.19 g,

12.82 mmol) to yield a slightly viscous bright orange oil **3** (> 99 %). Found 49.27; H, 4.95; $C_{10}H_{12}OS_3$ required C, 49.14; H, 4.95; ν_{max}/cm^{-1} 3315-2950 (broad), 2919, 2877, 1494, 1452, 1053, 1002, 797, 660; δ_H (400 MHz, $CDCl_3$) = 7.40-7.28 (5H, m, Ph), 4.69 (2H, s, C*H*$_2$-Ph), 3.91 (2H, t, S-C*H*$_2$-CH$_2$), 3.66 (2H, t, S-CH$_2$-C*H*$_2$), 2.38 (1H, br s, CH$_2$O*H*); δ_C (400 MHz, $CDCl_3$) = 224.1, 135.4, 129.9, 128.5, 61.2, 42.3, 39.8; *m*/*z* (EI) 245, 151.

Compound (**4**), benzyl 1-phenylethyl carbonotrithioate, was prepared in an analogous manner to that of compound (**1**) using benzyl mercaptan (0.50 g, 3.68 mmol), K_3PO_4 (0.78 g, 3.68 mmol), CS_2 (0.84 g, 11.03 mmol) and 1-bromoethyl benzene (0.68 g, 3.68 mmol). After addition of the halide the reaction mixture was stirred for four hours before working up to yield an orange oil **4** (91 %). Found C, 63.12; H, 5.32; $C_{16}H_{16}S_3$ required C, 63.11; H, 5.30; ν_{max}/cm^{-1} 3060, 3027, 2967, 1493, 1452, 1062, 799, 762, 669; δ_H (400 MHz, $CDCl_3$) = 7.32-7.16 (10H, m, Ph), 5.27 (1H, q, S-C*H*-CH$_3$), 4.52 (2H, s, S-C*H*$_2$-Ph), 1.69 (3H, d, S-CH-C*H*$_3$); δ_C (400 MHz, $CDCl_3$) = 221.4, 140.4, 134.3, 128.6, 128.1, 127.0, 49.7, 40.7, 20.7; *m*/*z* (EI) 305, 201.

Compound (**5**), cyanomethyl dodecyl carbonotrithioate, was prepared in a manner analogous to compound (**1**) using dodecane thiol (1.00 g, 4.94 mmol) and stirring with K_3PO_4 (1.05 g, 4.94 mmol) for one hour. CS_2 (1.02 g, 13.47 mmol) was added and stirring continued for one hour after which 2-bromopropionitrile (0.60 g, 4.49 mmol) was added. After halide addition reaction mixture was stirred for two hours. After work up a light brown/yellow oil **5** (71 %) was isolated with a distinctive odour. Found C, 57.77; H, 8.89; N, 4.35; $C_{16}H_{29}NS_3$ required C, 57.95; H, 8.81; N, 4.22;

ν_{max}/cm^{-1} 2954, 2919, 2851, 2241, 1468, 1102, 1074, 1048, 815, 719; δ_H (400 MHz, $CDCl_3$) = 4.84 (1H, q, CH_3CH-CN), 3.31 (2H, t, S-CH_2-CH_2), 1.63 (2H, m, S-CH_2-CH_2 and 3H, d, CH_3-CH-CN), 1.39-1.11 (18H, br, S-CH_2-CH_2-$(CH_2)_9$), 0.81 (3H, t, S-$(CH_2)_{11}$-CH_3); δ_C (400 MHz, $CDCl_3$) = 219.4, 119.0, 38.0, 32.8, 32.3, 30.0, 29.8, 29.7, 29.5, 28.8, 28.2, 23.1, 18.1, 14.5; *m/z* (EI) 396, 148, 136.

Compound (**6**), ethyl 2-(ethylthiocarbonothioylthio)-2-phenylacetate, was prepared in an analogous manner to compound (**5**) using dodecane thiol (1.00 g, 4.94 mmol) and K_3PO_4 (1.05 g, 4.94 mmol), CS_2 (1.02 g, 13.47 mmol) and ethyl α-bromophenyl acetate (1.09 g, 4.49 mmol), to yield a yellow/orange oil **6** (73 %). Found C, 62.73; H, 8.34; $C_{23}H_{16}O_2S_3$ required C, 62.68; H, 8.23; ν_{max}/cm^{-1} 2925, 2852, 1738, 1454, 1277, 1149, 1067, 1026, 815, 725, 694; δ_H (400 MHz, $CDCl_3$) = 7.40-7.22 (5H, m, Ph), 5.73 (1H, s, Ph-C*H*), 4.11 (2H, m, O-CH_2-CH_3), 3.24 (2H, t, S-CH_2-CH_2), 1.62 (2H, m, S-CH_2-CH_2), 1.38-1.09 (18H, br, S-CH_2-CH_2-$(CH_2)_9$ and 3H, t, O-CH_2-CH_3), 0.82 (3H, t, S-$(CH_2)_{11}$-CH_3); δ_C (400 MHz, $CDCl_3$) = 222.4, 169.3, 133.9, 129.4, 129.2, 129.0, 62.7, 58.4, 37.7, 32.3, 30.0, 29.9, 29.8, 29.5, 29.3, 28.3, 23.1, 14.5, 14.4; *m/z* (EI) 441, 291, 163.

Compound (**7**), ^{t}butyl dodecyl carbonotrithioate, was prepared in an analogous manner to that of compound (**1**) using ^{t}butyl thiol (1.00 g, 11.11 mmol) and stirring with K_3PO_4 (2.59 g, 12.22 mmol) and CS_2 (0.85 g, 33.33 mmol) for one hour. 1-bromododecane (2.92 g, 11.11 mmol) was added and stirred for 13 hours and worked up to yield a bright yellow/orange solid **7** (93 %). Found C, 61.10; H 10.32; $C_{17}H_{34}S_3$ required C, 61.01; H, 10.24; ν_{max}/cm^{-1} 2958, 2917, 2847, 1463, 1455, 1364, 1161,

1062, 1020, 807, 722; δ_H (400 MHz, $CDCl_3$) = 3.20 (2H, t, S-C*H*$_2$-$(CH_2)_{10}$-CH_3), 1.67-1.50 (9H, s, C-(C*H*$_3$)$_3$ and 2H, m, S-CH_2-C*H*$_2$), 1.11-1.39 (18H, t, S-$(CH_2)_2$-(C*H*$_2$)$_9$-CH_3), 0.80 (3H, t, S-CH_2-$(CH_2)_{10}$-C*H*$_3$); δ_C (400 MHz, $CDCl_3$) = 224.4, 54.50, 36.7, 32.3, 30.0, 29.9, 29.8, 29.7, 29.5, 29.4, 28.3, 23.1, 14.5; *m*/*z* (EI) 263, 174.

Compound (**8**), 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid, was prepared in an analogous manner to that of compound (**4**) using dodecane thiol (1.34 g, 6.59 mmol), K_3PO_4 (1.02 g, 6.59 mmol), CS_2 (1.37 g, 17.97 mmol) and 2-bromo isobutyric acid (1.00 g, 5.99 mmol). After the halide addition the reaction mixture was allowed to stir for 13 hours. The solvent was removed under reduced pressure and the residue was extracted into CH_2Cl_2 (2 x 100 ml) from 1M HCl (100 ml). The organic extracts were washed with water (100 ml) and brine (100 ml). The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica using ethyl acetate to yield a bright yellow oil **8** (83 %) that crystallized on standing. Found C, 56.18; H, 8.75; $C_{17}H_{32}O_2S_3$ required C, 56.00; H, 8.85; ν_{max}/cm^{-1} 2400-3200 (br), 2954, 2916, 2849, 1737, 1713, 1469, 1122, 1070, 815, 718; δ_H (400 MHz, $CDCl_3$) = 11.19 (1H, br s, COO*H*), 3.20 (2H, t, S-C*H*$_2$-$(CH_2)_{10}$-CH_3), 1.66 (6H, s, C-(C*H*$_3$)$_2$), 1.60-1.11 (20H, t, S-CH_2-(C*H*$_2$)$_{10}$-CH_3), 0.80 (3H, t, S-CH_2-$(CH_2)_{10}$-C*H*$_3$); δ_C (400 MHz, $CDCl_3$) = 221.2, 179.3, 56.2, 39.7, 37.5, 32.3, 30.0, 29.7, 29.6, 29.5, 29.4, 28.9, 28.3, 25.6, 23.1, 14.5; *m*/*z* (EI) 365, 245, 169.

Compound (**9**) (1,3-dioxoisoindolin-2-yl)methyl dodecyl carbonotrithioate was prepared in an analogous manner to compound **4** by stirring dodecanethiol (0.93 g, 4.58 mmol) in a suspension of K_3PO_4 (1.72 g, 8.09 mmol) in acetone (20 ml) for

forty minutes. CS_2 (0.95 g, 12.50 mmol) was added and the solution turned bright yellow. After stirring for thirty minutes *N*-bromomethyl phthalimide (1.00 g, 4.17 mmol) was added and an instant precipitation was noted requiring the addition of a portion of acetone (10 ml). After stirring for thirty minutes the suspension was filtered and the cake was washed with acetone (2 x 20 ml). After removing the solvent from the filtrate under reduced pressure the resulting yellow residue was recrystallized from hot ethyl acetate to yield fine bright yellow crystals **9** (59 %). Found C, 60.39; H, 7.19; N, 3.10; $C_{22}H_{31}NO_2S_3$ required 60.37; H, 7.14; N, 3.20; ν_{max}/cm^{-1} 2953, 2916, 2848, 1711, 1379, 1064, 912, 704; δ_H (400 MHz, $CDCl_3$) = 7.90 (2H, m, 2Ph-*H*), 7.76 (2H, m, 2Ph-*H*), 5.65 (2H, s, S-C*H*$_2$-N), 3.39 (2H, t, S-C*H*$_2$-CH$_2$), 1.66 (2H, q, S-CH$_2$-C*H*$_2$-CH$_2$), 1.44-1.26 (18H, br, S-CH$_2$-CH$_2$-(C*H*$_2$)$_9$-CH$_3$), 0.91 (3H, t, CH$_2$-C*H*$_3$). δ_C (400 MHz, $CDCl_3$) = 218.9, 164.7, 145.1, 132.5, 130.0, 121.8, 40.1, 35.4, 30.0, 27.7, 27.6, 27.5, 27.4, 27.2, 27.0, 25.9, 22.9, 20.8, 11.2; *m*/*z* (EI) 438, 362, 210, 160.

Compound (**10**), *O*-ethyl-*S*-1-phenylethyl carbonodithioate, was prepared by stirring Cs_2CO_3 (5.29 g, 16.22 mmol) in ethanol (50 ml) for 2 hours. CS_2 (1.23 g, 16.22 mmol) was added and the solution slowly turned yellow. After stirring for 2 hours 1-bromo ethyl benzene (1.00g g, 5.41 mmol) was added. After stirring for 4 hours the suspension was filtered and the cake was washed with acetone (20 ml) and CH_2Cl_2 (20 ml). After removing the solvent from the filtrate under reduced pressure the resulting yellow/green residue was dissolved in CH_2Cl_2 (100 ml) and extracted with a saturated brine solution (2 x 100 ml). The solvent was removed from the organic layer under reduced pressure and the residue was purified by column chromatography on silica using a petroleum ether/ethyl acetate gradient to yield a very light green/yellow

oil **10** (73 %). Found C, 58.39; H, 6.24; $C_{11}H_{14}OS_2$ required C, 58.37; H, 6.23; ν_{max}/cm^{-1} 3029, 2978, 2866, 1492, 1452, 1207, 1145, 1109, 1036, 1024, 763, 696; δ_H (400 MHz, $CDCl_3$) = 7.52-7.31 (5H, m, Ph), 5.05 (1H, q, C*H*-CH_3), 4.72 (2H, q, O-C*H*$_2$-CH_3), 1.83 (3H, d, CH-C*H*$_3$), 1.46 (3H, t, O-CH_2-C*H*$_3$); δ_C (400 MHz, $CDCl_3$) = 213.6, 142.3, 128.9, 128.0, 70.2, 49.8, 44.3, 22.3, 14.3; *m*/*z* (EI) 226, 185, 132.

Compound (**11**), *S*-benzyl-*O*-isopropyl carbonodithioate, was prepared in an analogous manner to that of compound (**10**) using Cs_2CO_3 (4.62 g, 14.16 mmol) in isopropyl alcohol (50 ml), CS_2 (1.08 g, 14.15 mmol) and benzyl bromide (1.00 g, 4.72 mmol). Yielding a very light green/yellow oil **11** (97 %). Found C, 58.60; H, 6.20. $C_{11}H_{14}OS_2$ required C, 58.37; H, 6.23; ν_{max}/cm^{-1} 3062, 2980, 2933, 1495, 1373, 1223, 1086, 1031, 901, 695; δ_H (400 MHz, $CDCl_3$) = 7.41-7.27 (5H, m, Ph), 5.81 (1H, m, C*H*$(CH_3)_2$), 4.39 (2H, s, C*H*$_2$-Ph), 1.42 (6H, d, CH(C*H*$_3$)$_2$); δ_C (400 MHz, $CDCl_3$) = 211.8, 134.4, 127.6, 127.2, 126.1, 76.6, 38.8, 19.9; *m*/*z* (EI) 226, 185. 131.

Compound (**12**), ethyl 2-(ethoxycarbonothioylthio)propanoate, was prepared in an analogous manner to that of compound (**10**) using Cs_2CO_3 (5.40 g, 16.57 mmol), CS_2 (1.26 g, 16.57 mmol) in ethanol (50ml) and 1-ethyl-2-bromo propionate (1.00 g, 5.53 mmol). After halide addition the reaction mixture was stirred for 13 hours to yield a light green/yellow oil **12** (72 %). Found C, 43.58, H, 6.39; $C_8H_{14}O_3S_2$ required C, 43.22; H, 6.35; ν_{max}/cm^{-1} 2982, 2937, 1732, 1448, 1366, 1214, 1159, 1111, 1056, 858; δ_H (400 MHz, $CDCl_3$) = 4.40 (1H, q, CH_3-C*H*-S), 4.16 (2H, q, (CO)-O-C*H*$_2$-CH_3), 3.97 (2H, q, (CS)-O-C*H*$_2$-CH_3), 1.32 (3H, d, CH-C*H*$_3$), 1.17 (3H, t, (CO)-O-CH_2-

C*H*$_3$), 1.03 (3 H, t, (CS)-O-CH$_2$-C*H*$_3$); δ_C (400 MHz, $CDCl_3$) = 213.3, 171.8, 70.6, 62.1, 47.6, 17.3, 14.5, 14.1; *m*/*z* (EI) 223, 177, 135.

Compound (**13**), benzyl diisopropylcarbamodithioate, was prepared by stirring diisopropylamine (1.00 g, 9.90 mmol) with Cs_2CO_3 (3.23 g, 9.90 mmol) in acetone (20 ml) for 20 minutes then CS_2 (3.23 g, 9.90 mmol) was added and stirring continued for 2 hours. Benzyl bromide (2.26 g, 29.7 mmol) was added and an immediate precipitate was noticed. After stirring for ten minutes the reaction mixture was filtered and the cake was washed with acetone (20 ml) and CH_2Cl_2 (20 ml). After the solvent was removed under reduced pressure the residue was purified by column chromatography on silica using a petroleum ether/ethyl acetate gradient (prior to loading column silica was washed with solvent containing 1% triethylamine to stop degradation of product on column) yielding a light green oil **13** (61 %) that crystallized on refrigeration. Found C, 62.88; H, 7.90; N, 5.17; $C_{14}H_{21}NS_2$ required C, 62.88; H, 7.91; N, 5.24; ν_{max}/cm^{-1} 3061, 3028, 2930, 2968, 1476, 1438, 1371, 1311, 1197, 1187, 1138, 1029, 710, 693; δ_H (400 MHz, $CDCl_3$, -40 °C) = 7.43-7.22 (5H, m, Ph-*H*), 6.22 (0.3H, m, N-C*H*$(CH_3)_2$), 4.99 (0.7H, m, N-C*H*$(CH_3)_2$), 4.58 (0.6H, s, S-C*H*$_2$-Ph), 4.18 (0.3H, m, N-CH(C*H*$_3$)$_2$), 4.04 (0.7H, m, N-CH(C*H*$_3$)$_2$), 3.91 (1.4H, s, S-C*H*$_2$-Ph), 1.71 (3.9H, d, N-CH(C*H*$_3$)$_2$), 1.54-1.35 (2.3H, br d, N-C*H*$(CH_3)_2$), 1.28 (3.9H, d, N-CH(C*H*$_3$)$_2$), 1.26 (1.9H, d, N-C*H*$(CH_3)_2$); δ_C (400 MHz, $CDCl_3$, -40 °C) = 197.6, 193.8, 137.5, 130.7, 129.6, 128.4, 68.0, 57.3, 56.3, 52.8, 50.7, 49.5, 43.2, 41.5, 21.1, 19.7, 19.2; *m*/*z* (EI) 268, 144.

Compound (**14**), benzyl methyl(phenyl)carbamodithioate was prepared in a manner analogous to compound (**10**) using *N*-methylaniline (1.00 g, 5.92 mmol), K_3PO_4 (1.93 g, 5.92 mol), CS_2 (1.35 g, 17.75 mmol) and benzyl bromide (1.01 g, 5.92 mmol), after CS_2 addition reaction mixture was stirred for 6 hours) to yield a yellow oil **14 (**70 %). Found C, 65.97; H, 5.83; N, 5.43; $C_{15}H_{15}NS_2$ required C, 65.89; H, 5.53; N, 5.12; ν_{max}/cm^{-1} 3061, 3026, 2894, 2814, 1598, 1505, 1451, 1353, 1212, 1115, 944, 747, 727, 690. δ_H (400 MHz, $CDCl_3$) = 7.52-7.64 (2 H, m, Ph-*H meta* to N), 7.52-7.45 (5H, m, Ph), 6.91-7.07 (3H, m, Ph-*H ortho* and *para* to N), 4.73 (2H, s, S-C*H*$_2$-Ph), 3.22 (3H, s, N-C*H*$_3$); δ_C (400 MHz, $CDCl_3$) = 219.4, 133.3, 129.6, 129.2, 127.3, 127.2, 117.0, 112.8, 57.1, 38.9; *m*/*z* (EI) 228, 199, 198, 132.

Compound (**15**), 1-phenylethyl 1H-imidazole-1-carbodithioate was prepared in a manner analogous to compound (**13**) using imidazole (0.20 g, 2.94 mmol), K_3PO_4 (0.63 g, 2.94 mmol), CS_2 (0.67 g, 8.82 mmol) and 1-bromo-ethyl-benzene (0.20 g, 2.94 mmol). After halide addition reaction mixture was stirred for 4 hours and worked up to yield a viscous slightly brown/yellow oil **15** (78 %). Found C, 57.63; H, 4.94; N, 11.08; $C_{12}H_{12}N_2S_2$ required C, 58.03; H, 4.87; N, 11.28. ν_{max}/cm^{-1} 3118, 2969, 2925, 1464, 1365, 1267, 1215, 1040, 1001, 810, 695; δ_H (400 MHz, $CDCl_3$) = 8.35 (1H, s, imidazole), 7.65 (1H, s, imidazole), 7.15-7.35 (5H, m, Ph), 7.00 (1H, s, imidazole), 5.1 (1 H, q, CH_3-C*H*), 1.75 (3H, d, C*H*$_3$-CH); δ_C (400 MHz, $CDCl_3$) = 206.7, 140.4, 136.0, 131.8, 129.2, 128.6, 128.2, 118.1, 51.4, 21.5; *m*/*z* (EI) 249, 173.

Compound (**16**), 4-(1-(tert-butyl(2-methyl-1-phenylpropyl)aminooxy)ethyl)benzyl dodecyl carbonotrithioate was prepared in a manner analogous to compound (**4**) using dodecane thiol (0.60 g, 2.68 mmol), K_3PO_4 (0.46 g, 2.68 mmol), CS_2 (0.60 g,

8.04 mmol) and *N*-^{t}butyl-O-(1-(4-(chloromethyl)phenyl)ethyl)-*N*-(2-methyl-1-phenylpropyl)hydroxylamine (1.00 g, 2.68 mmol). After halide addition the reaction mixture was stirred for 13 hours. Yielding **16** (87 %) as an extremely viscous yellow oil. Found C, 70.26; H, 9.45, N, 2.28; $C_{36}H_{57}NOS_3$ required C, 70.19; H, 9.33; N, 2.27; ν_{max}/cm^{-1} 2956, 2923, 2853, 1453, 1361, 1206, 1060, 811, 700; δ_H (400 MHz, $CDCl_3$) = 7.49- 7.01 (9H, m, Ph), 4.98-4.97 (1H, m, CH_3CH), 4.60 (2H, s, CH_2), 3.49-3.43 (1 H, d, NC*H*, diastereoisomer A and 2H, t, S-CH_2-CH_2), 3.34 (1H, d, NC*H*, diastereoisomer B), 2.39-2.38 (1H, m, $CH(CH_3)_2$), 1.72 (2H, m, S-CH_2-CH_2) 1.66 (3H, d, diastereoisomer A), 1.58 (3H, d, diastereoisomer B), 1.47-1.19 (3H, d, diastereoisomer and 18H, m, S-CH_2-CH_2-$(CH_2)_9$), 1.08 (9H, s, $C(CH_3)_3$, diastereoisomer A), 0.94 (3H, d, diastereoisomer B), 0.87 (3H, t, S-$(CH_2)_{11}$-CH_3), 0.82 (9H, s, $C(CH_3)$, diastereoisomer B), 0.57 (3H, d, diastereoisomer A), 0.25 (3H, d, diastereoisomer B); δ_C (400 MHz, $CDCl_3$) = 146.2, 142.5, 135.9, 131.1, 128.5, 127.5, 126.6, 83.3, 77.3, 60.6, 46.3, 32.1, 31.0, 28.3, 24.8, 22.1, 21.3.

Synthesis of PS-*co*-PS-RAFT, 17 and subsequent grafting

A mixture of the alkoxyamine[1] (2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane) (33 mg, 0.10 mmol), styrene (1.06 g, 10.0 mmol), and 4-vinyl benzyl chloride (0.15 g, 1.00 mmol) were degassed by three freeze/pump/thaw cycles, sealed under argon, and heated at 120 °C for 3 h. The solidified reaction mixture was then re-dissolved in THF (5 ml) and precipitated into MeOH (2× 100 ml) at 4 °C. The precipitate was collected by vacuum filtration and dried overnight in *vacuo*, to give the precursor copolymer as a white solid (0.90 g, 74 % yield), M_n^{NMR} = 10,600 g/mol (12.1 % incorporation of Cl functionality), M_n^{GPC} = 10,300 g/mol, M_w/M_n = 1.13. A

portion of this solid (0.50 g, 0.60 mmol Cl functionality) was then dissolved in acetone (30 ml) and imidazole (0.06 g, 0.90 mmol) and then K_3PO_4 (0.19 g, 0.90 mmol) were added. The mixture was allowed to stir for 5 minutes and then CS_2 (0.14 g, 1.8 mmol) was added. The reaction mixture was stirred at room temperature overnight and then filtered and reduced to dryness. The solid was then dissolved in 5 ml of THF and precipitated three times into hexane (200 ml) at 4 °C. The precipitate was collected by vacuum filtration and dried overnight in *vacuo*, to give the desired RAFT functionalised polymer, **17**, as a yellow solid (0.47 g, 86 %), M_n^{NMR} = 11,700 g/mol, M_n^{GPC} = 12,100 g/mol, M_w/M_n = 1.15. δ_H (400 MHz, $CDCl_3$) = 8.4-8.3 (imidazole end group), 7.7-7.6 (imidazole end group), 7.2-6.2 (m, Ph-*H*), 4.8-4.6 (br, C*H*$_2$SCS-imidazole), 2.2-2.0 (br, C*H* of the polymer backbone), 1.8-1.3 (br, C*H*$_2$ of the polymer backbone).

Starting block, **17** (0.50 g, 0.50 mmol of RAFT functionality) was dissolved in *t*-butyl acrylate (6.35 g, 50.0 mmol), dioxane (1.0 ml) and AIBN (0.008 g, 0.05 mmol) and degassed by three freeze/pump/thaw cycles, sealed under argon, and heated at 60 °C for 16 h. The solidified reaction mixture was then re-dissolved in THF (5 ml) and precipitated twice into H_20/MeOH (1:1 v/v, 100 ml) at 4 °C. The precipitate was collected by vacuum filtration and dried overnight in vacuo, to give the desired graft copolymer **18**, as a pale yellow solid (1.2 g, 18 %), M_n^{NMR} = 28,300 g/mol, M_n^{GPC} = 19,900 g/mol, M_w/M_n = 1.23.

Typical ^{t}BuA polymerisation.

^{t}Butyl acrylate (1.00 g, 7.87 mmol), CTA (**1**) (0.011 g, 0.039 mmol), and AIBN (0.0006 g, 0.004 mmol) were dissolved in dioxane (1.14 ml). The solution was transferred to a clean dry ampoule equipped with a stirrer bar and the solution

thoroughly degassed using three freeze-pump-thaw cycles. The ampoule was placed in an oil bath at 60 °C and heated for 24 hours. After quenching in liquid nitrogen and diluting with THF the polymer was precipitated into a cold solution of H_2O/MeOH (1:10 v/v). After decanting off the solvent the resulting gummy polymer was redissolved in THF and dried over $MgSO_4$. The drying agent was removed under gravity filtration and the solvent was removed from the filtrate under reduced pressure to yield a crystalline solid.

Table S1 - Polymerisation data for purified and unpurified symmetrical CTA

CTA	Conversion by NMR (%)	M_n (Da)	M_w/M_n
1	> 99	24 500	1.18
1a	> 99	24 000	1.18

Typical styrene polymerisation

Styrene (1.00 g, 9.62 mmol), CTA **2** (0.042 g, 0.096 mmol), and solvent, if required were transferred to a clean dry glass ampoule equipped with a stirrer bar and the solution thoroughly degassed using three freeze-pump-thaw cycles. The ampoule was placed in an oil bath at 110 °C and heated for 22.5 hours. After quenching in liquid nitrogen and diluting with THF the polymer was precipitated into cold methanol. The resulting solids were dried under vacuum and characterised.

Typical MMA polymerisation

MMA (1.00 g, 10.3 mmol), CTA (**7**) (0.012 g, 0.035 mmol), and AIBN (0.0005 g, 0.0034 mmol) were transferred to a clean dry ampoule equipped with a stirrer bar and the solution thoroughly degassed using three freeze-pump-thaw cycles. The ampoule

was placed in an oil bath at 90 °C and heated for the required polymerisation time. After quenching in liquid nitrogen and diluting with THF the polymer was precipitated into petroleum ether. After filtering the gummy solid was redissolved into THF and then the solvent was removed under reduced pressure to yield a crystalline solid.

Typical VAc polymerisation

VAc (1.00 g, 11.36 mmol), CTA (**12**) (0.025 g, 0.114 mmol), and AIBN (0.0093 g, 0.057 mmol) were transferred to a clean dry ampoule equipped with a stirrer bar and the solution thoroughly degassed using three freeze-pump-thaw cycles. The ampoule was placed in an oil bath at 80 °C and heated for 13 hours. After quenching in liquid nitrogen and diluting with THF the polymer was precipitated into petroleum ether. After decanting the solvent, the gummy solid was redissolved into THF and then the solvent was removed under reduced pressure to yield a crystalline solid.

Typical NVC polymerisation

NVC (1.00 g, 5.18 mmol), CTA (**10**) (0.012 g, 0.052 mmol), and AIBN (0.0009 g, 0.0052 mmol) were dissolved in dioxane (1 ml) and transferred to a clean dry ampoule equipped with a stirrer bar and the solution thoroughly degassed using three freeze-pump-thaw cycles. The ampoule was placed in an oil bath at 90 °C and heated for the required polymerisation time. After quenching in liquid nitrogen and diluting with THF the polymer was precipitated into petroleum ether then isolated as a crystalline solid by filtration.

Table S2 – Polymerisation data for a range of CTAs and monomers

CTA	Monomer	Reaction time (hrs)	Conversion by NMR (%)	M_n th (NMR)	M_n (Da)	M_w/M_n
4	St	21.5	80	8,400	6 800	1.08
9	St	21.5	76	7 900	6 200	1.07
5	^{t}BuA	20.0	99	12 800	12 300	1.13
7	MMA	3.5	> 99	29 200	49 900	1.37
10	VAc	13.0	> 99	8 900	8 900	1.62
12	VAc	1.5	89	8 100	7 700	1.55
11	NVC*	22.5	78	15 300	7 000	1.34

* denotes 1:1 $^v/_v$ with dioxane

Reference

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