Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Examining the UV-vis Absorption of RAFT Chain Transfer Agents, and Their Use for Polymer Analysis

Katja Skrabania,[1] *Anna Miasnikova,*[1] *Achille Mayelle Bivigou-Koumba,*[1] *Daniel Zehm,*[1] *and André Laschewsky**[1,2]

[1]Department of Chemistry, Universität Potsdam, D-14476 Potsdam-Golm

[2]Fraunhofer Institute for Applied Polymer Research, D-14406 Potsdam-Golm

Email: laschews@rz.uni-potsdam.de

Synthesis of the RAFT Agents.

Naphth-2-ylmethyl dithiobenzoate (CTA2).

The RAFT agent was synthesized by alkylation of the dithioacid salt according to a general procedure.[1] Under nitrogen, 2.66 g (35 mmol) of CS_2 were added slowly to 16.5 ml (33 mmol) of phenylmagnesium chloride solution (2 M in THF) at ambient temperature. 11.21 g (50 mmol) of 2-bromomethyl naphthalene dissolved in 10 mL of THF were added at 30°C within 15 min. After maintaining the reaction mixture for 2 h at 50°C, 250 mL of cold water were added and the organic products were extracted in two portions with 300 mL of diethyl ether. The ether phase was washed with 250 mL of brine, dried over anhydrous $MgSO_4$ and concentrated. According to thin layer chromatography (*n*-hexane/CH_2Cl_2, 4:1 by volume) the raw material contained at least six by-products. The removal of all impurities necessitated two successive purification steps by column chromatography (silica gel 60, 0.040-0.063 mm) using first cyclohexane and then *n*-hexane/CH_2Cl_2 (4:1 by volume) as the eluent. Only fractions that were pure according to TLC were collected and combined. After removal of the solvent in vacuo the pure product was obtained as red solid (0.96 g). m.p. 84°C. Elemental analysis ($C_{18}H_{14}S_2$, M_r = 294.43): Calc: C 73.43, H 4.79, S 21.78. Found: C 73.82, H 4.81, S 20.15. MS (EI, negative ions): m/z = 294. ^{1}H NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 4.78 (s, 2H, C<u>H</u>$_2$-aryl), 7.36-7.41 (t, 2H, C(3)<u>H</u> phenyl), 7.47-7.56 (m, 1H + 3H, C(4)<u>H</u> phenyl, naphthyl), 7.82-7.88 (m, 4H, naphthyl), 8.02-8.04 (d, 2H, C(2)<u>H</u> phenyl). ^{13}C NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 42.5 (-<u>C</u>H$_2$-aryl), 126.1, 126.4, 126.9, 127.0, 127.7, 128.2, 128.3, 128.5 (<u>C</u>H aryl), 132.4, 132.8, 133.3 (C aryl), 144.8 (<u>C</u>(1) phenyl), 227.5 (-C(=S)-S-). FT-IR (KBr, selected bands, wavenumber in cm^{-1}): 3053, 1593, 1444, 1225, 1041, 889, 822, 756.

1H-perimidine 2-dithiocarbonic acid benzyl ester (**CTA3**). The title compound was prepared according to a modified procedure by W. Thiel et al.[2]

(i) 2-chloromethyl-1H-perimidinium chloride. To a solution of 5.0 g (31.6 mmol) of 1,8-diaminonaphthalene in 32 ml of anhydrous toluene were added dropwise 3.66 g (32.4 mmol) of chloroacetyl chloride dissolved in 7.8 ml of anhydrous toluene. A yellow precipitate formed immediately. After complete addition the reaction mixture was refluxed for several minutes. The product was collected by vacuum filtration of the warm reaction mixture and washed with toluene and *n*-hexane. 7.9 g (98%) of a yellow powder were obtained. The intermediate product was not purified further but used directly for the synthesis of the dithio compound.

(ii) Coupling to yield 1H-perimidine dithiocarbonic acid benzyl ester. Perimidinium hydrochloride (4.0 g, 15.7 mmol) was added to a mixture of S_8 (1.01 g, 31.5 mmol) and triethylamine (6.40 g, 63.3 mmol) in 22 ml of anhydrous DMF under vigourous stirring, while keeping the temperature of the

solution at 40°C. After stirring for another 2 h at ambient temperature, the reaction mixture was cooled to 0-5°C and benzyl bromide (2.97 g, 17.4 mmol) was added dropwise. Precipitate was removed by vacuum filtration, and the dithioester was precipitated from the deep blue filtrate by adding slowly 16 ml of water. The product was collected by vacuum filtration and washed with 16 ml of cold ethanol. Deep blue shiny crystals (5.7 g, 92%) were obtained. Elemental analysis ($C_{19}H_{14}N_2S_2$, M_r = 334.46): Calc: C 68.23, H 4.22, N 8.38 S 19.17 Found: C 67.67, H 4.35, N 8.44, S 19.18. MS (EI, negative ions): m/z = 334. ^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 4.43 (s, 2H, -C<u>H</u>$_2$-aryl), 6.24-6.27 (quart, 1H, C(9)H perimidinyl), 6.87-6.90 (quart, 1H, C(4)H perimidinyl), 7.02-7.09 (m, 2H, C(5)H, C(8)H perimidinyl), 7.14-7.23 (m, 2H, C(6)H, C(7)H perimidinyl), 7.30-7.40 (m, 5H, phenyl). ^{13}C-NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 41.98 (-C<u>H</u>$_2$-aryl), 102.86, 117.46, 119.16, 122.55, 127.93, 128.74, 129.47, 134.02, 135.63, 143.34, 148.52 (C(2)perimidinyl). (75 MHz in *d*6-DMSO, δ in ppm): δ = 121.31, 122.50, 127.59, 128.51, 129.27, 134.54, 135.01, 151.00 (C(2)perimidinyl), 219.17 (-C(=S)-S-).

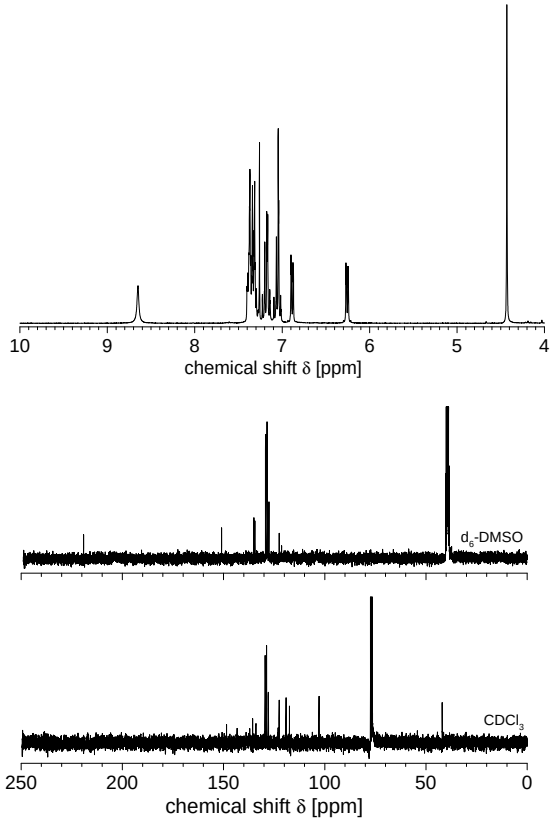

Figure S1: NMR spectra of **CTA3**. From top to bottom: ^{1}H NMR spectrum in $CDCl_3$, ^{13}C NMR spectrum in DMSO-*d*6, ^{13}C NMR spectrum in $CDCl_3$.

Butyl 2-(butylsulfanylthiocarbonylsulfanyl) propionate (CTA6).

(i) Butyl 2-bromo-propionate. Triethylamine (13 mL, 94 mmol) and 1-butanol (8.5 g, 115 mmol) were mixed with 100 mL of CH_2Cl_2 in a 500 ml-round bottom flask equipped with a stir bar and a rubber septum. The mixture was cooled to 0°C and 10 mL (95 mmol) of 2-bromopropionyl bromide were added dropwise under stirring. The reaction mixture was maintained at 0°C for 30 min and then stirred at ambient temperature over night. The precipitated triethylammonium bromide was filtered off and washed with CH_2Cl_2. The collected organic phases were washed with dilute HCl and brine. After drying over $MgSO_4$ and evaporation of the solvent, the crude product was obtained as light yellow oil. Vacuum distillation at 65°C (2 mbar) gave 13.7 g (69%) of a colorless liquid. ^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 0.92 (t, 3H, C<u>H</u>$_3$-CH$_2$-), 1.32-1.44 (m, 2H, -O-C-C-C<u>H</u>$_2$), 1.58-1.67 (m, 2H, -O-C-C<u>H</u>$_2$-), 1.80 (d, 3H, -CHBr(C<u>H</u>$_3$)-), 4.08-4.21 (m, 2H, -O-CH$_2$-), 4.31-4.38 (m, 1H, -C<u>H</u>Br-). ^{13}C-NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 13.6 (<u>C</u>H$_3$-CH$_2$-), 18.9 (-O-C-C-<u>C</u>H$_2$-), 21.6 (-CHBr(<u>C</u>H$_3$)-), 30.4 (-O-C-<u>C</u>H$_2$-), 40.2 (-<u>C</u>HBr(CH$_3$)-), 65.7 (-O-CH$_2$-), 170.2 (-C(=O)-O-).

(ii) Coupling to butyl 2-(butylsulfanylthiocarbonylsulfanyl) propionate. Under nitrogen flow, 4.98 g (62.2 mmol) of a 50 wt% aqueous solution of NaOH were added to 5.61 g (62.2 mmol) of 1-butanethiol dissolved in 30 mL of THF. Upon dropwise addition of 4.74 g (62.2 mmol) of CS_2, the white suspension became a clear, bright yellow solution. The reaction mixture was stirred for additional 10 min before 13.0 g (62.3 mmol) of butyl 2-bromo-propionate were added within 10 min. The reaction mixture was stirred at ambient temperature over night. To the reaction mixture were added 100 mL of water and the aqueous phase was extracted twice with 100 mL of *n*-hexane. The combined hexane phases were washed with water and dried with anhydrous $MgSO_4$. After evaporation of the solvent the crude product was obtained as orange-colored oil (17.0 g) which did not crystallize in the cold (4°C). The crude product contained two by-products according to TLC. As Kugelrohr distillation led to decomposition, a fraction (3.7 g) of the raw material was purified by column chromatography (silicagel 60, Merck, 0.040-0.063 mm, eluent: *n*-hexane). Yield: 3.1 g (79%). Elemental analysis ($C_{12}H_{22}O_2S_3$, M_r = 294.50): Calc: C 48.94, H 7.53, S 32.66. Found: C 48.75, H 7.47, S 31.73. MS (EI, negative ions): m/z = 294. ^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 0.92 (t, 3H + 3H, C<u>H</u>$_3$-CH$_2$-), 1.31-1.48 (m, 2H + 2H, CH$_3$-C<u>H</u>$_2$-), 1.57-1.72 (m, 2H + 2H + 3H, -O-C-C<u>H</u>$_2$-, -S-C-C<u>H</u>$_2$-, -S-CH(C<u>H</u>$_3$)-), 3.36 (t, 2H, -S-C<u>H</u>$_2$-), 4.13 (t, 2H, -O-C<u>H</u>$_2$-), 4.81 (q, 1H, -S-C<u>H</u>(CH$_3$)-). ^{13}C-NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 13.5 (-O-C-C-C-<u>C</u>H$_3$; -S-C-C-C-<u>C</u>H$_3$), 16.9 (-S-CH(<u>C</u>H$_3$)-), 19.0 (-O-C-C-<u>C</u>H$_2$-), 22.0 (-S-C-C-<u>C</u>H$_2$-), 29.9 (-S-C-<u>C</u>H$_2$-), 30.5 (-O-C-<u>C</u>H$_2$-), 36.8 (-S-<u>C</u>H$_2$-), 48.0 (-S-<u>C</u>H(CH$_3$)-), 65.6 (-O-<u>C</u>H$_2$-), 171.1 (-C(=O)-O-), 222.0 (-S-C(=S)-S-). FT-IR (KBr, selected bands, wavenumber in cm^{-1}): 2958, 2931, 2872, 1732, 1455, 1378, 1305, 1247, 1159, 1056, 812.

2-(*n*-Butylsulfanylthiocarbonylsulfanyl)-propionic acid 2-(2-methoxy-ethoxy)-ethyl ester (CTA7)

(i) 2-Bromo-propionic acid 2-(2-methoxy-ethoxy)-ethyl ester. Triethylamine (2.4 g, 24 mmol) and diethylene glycol monomethylether (3.4 g, 28 mmol) were mixed with 25 mL of dry dichloromethane and cooled to 0ºC. 2-bromopropionyl bromide (2.4 mL, 23 mmol, d = 2.035 g/mL) was added dropwise. The reaction mixture was maintained at 0°C for 30 min and then stirred at ambient temperature over night. The precipitated triethylammonium bromide was filtered off and washed with CH_2Cl_2. The collected organic phases were washed with 1M HCl solution and brine. After drying over $MgSO_4$ and evaporation of the solvent, the crude product was obtained as light yellow oil. Vacuum distillation at 150°C (2 mbar) gave 4.3 g (73 %) of colourless liquid. ^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 1.82 (d, 3H, Br-CH-$\underline{CH_3}$), 3.38 (s, 3H, $\underline{CH_3}$-O-), 3.53-3.56 (m, 2H, CH_3-O-$\underline{CH_2}$-), 3.64-3.67 (m, 2H, O-CH_2-$\underline{CH_2}$-O-), 3.73 (t, 2H, -CH_2-O-$\underline{CH_2}$-CH_2-), 4.33 (t, 2H, -CH_2-O-CH_2-$\underline{CH_2}$-OOC-), 4.40 (q, 1H, Br-$\underline{CH}$-CH_3).

(ii) 2-(n-butylsulfanylthiocarbonylsulfanyl)-propionic acid 2-(2-methoxy-ethoxy)-ethyl ester. Triethyl-amine (1.2 mL, 8.5 mmol, d = 0.73 g/mL) and 1-butanedithiol (0.7 mL, 6.5 mmol, d = 0.84 g/mL) were mixed with 10 mL of methyl *tert*-butyl ether and purged with nitrogen for 15 min. The dropwise addition of 0.5 mL (8.8 mmol, d = 1.262 g/mL) of CS_2 at room temperature, gave a clear, bright yellow solution. After 30 min of stirring, 1.5 g (5.9 mmol) of 2-Bromo-propionic acid 2-(2-methoxy ethoxy)-ethyl ester were added dropwise and the mixture allowed to react over night. 20 mL of water were added and the mixture was extracted two times with 20 mL of hexane. The combined hexane phases were dried over anhydrous $MgSO_4$ and the solvent evaporated. According to TLC (silica gel, hexane/ethyl acetate: 1/1), the crude product contained by-products and was purified by column chromatography (silicagel 60, Merck, 0.040-0.063 mm, eluent: hexane/ethyl acetate: 1/1) to give a dark orange oil. Yield: 1.1 g (55 %). Elemental analysis: ($C_{13}H_{24}O_4S_3$ M_w = 340.52): Calculated: C 45.85, H 7.10, S 28.25 Found: C 46.06, H 7.14, S 27.24 ; MS (EI, negative ions): m/z = 340. ^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 0.92 (t, 3H, $\underline{CH_3}$-CH_2-), 1.36-1.48 (m, 2H, CH_3-$\underline{CH_2}$-CH_2-), 1.59 (d, 3H, $\underline{CH_3}$-CH-S-), 1.62-1.72 (m, 2H, CH_3-CH_2-$\underline{CH_2}$-), 3.35 (t, 2H, -S-$\underline{CH_2}$-CH_2-), 3.37 (s, 3H, $\underline{CH_3}$-O-), 3.52-3.55 (m, 2H, CH_3-O-$\underline{CH_2}$-), 3.60-3.64 (m, 2H, O-CH_2-$\underline{CH_2}$-O-), 3.69 (t, 2H, -CH_2-O-$\underline{CH_2}$-CH_2-), 4.29 (t, 2H, -CH_2-O-CH_2-$\underline{CH_2}$-OOC-), 4.83 (q, 1H, CH_3-$\underline{CH}$-S-). ^{13}C-NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 13.4 ($\underline{CH_3}$-CH_2-), 16.8 ($\underline{CH_3}$-CH-S-), 21.9 (CH_3-$\underline{CH_2}$-CH_2-), 29.8 (CH_3-CH_2-$\underline{CH_2}$-), 36.8 (-S-$\underline{CH_2}$-CH_2-), 47.8 (CH_3-$\underline{CH}$-S-), 58.9 ($\underline{CH_3}$-O-), 64.75 (-CH_2-O-CH_2-$\underline{CH_2}$-O-), 68.8 (-CH_2-O-$\underline{CH_2}$-CH_2-), 70.4 (-O-CH_2-$\underline{CH_2}$-O-), 71.8 (CH_3-O-$\underline{CH_2}$-), 170.9 (CH-$\underline{C}$OO-CH_2).

***N,N*-dimethyl 2-(butylsulfanylthiocarbonylsulfanyl) propionamide (CTA9).**

(i) N,N-dimethyl 2-bromopropionamide with N,N-dimethyl 2-chloropropionamide as by-product. The title compound was synthesized according to the procedure by Rademacher et al.[3] To a stirred suspension of 9.4 g (115 mmol) of dimethylamine hydrochloride in 150 mL of CH_2Cl_2 were added 26 mL (187 mmol) of Et_3N at 0 °C. After the hydrochloride dissolved almost completely, 2-bromopropionylbromide (10 mL, 95 mmol) was added dropwise and a white suspension formed. The reaction was maintained for 30 min at 0 °C and stirred for 2 h at ambient temperature. The precipitated triethylammonium bromide and chloride was filtered off and washed with CH_2Cl_2. The collected organic phases were dried over $MgSO_4$ and the solvent was evaporated in vacuo to afford the product as yellow oil. Vacuum distillation at 85°C (1.0 mbar) gave 11.21 g of a colorless liquid. ^{1}H and ^{13}C NMR spectra of the distilled product showed signals, which could not be attributed to the title compound, but which were attributed to N,N-dimethyl 2-chloropropionamide formed as by-product, presumably due to Finkelstein halogen exchange reaction. According to the integrated signals of the ^{1}H NMR spectrum, the molar ratio of mixture of N,N-dimethyl 2-bromopropionamide and N,N-dimethyl 2-chloropropionamide was 3/1. This mixture was engaged in the subsequent alkylation reaction to obtain the final product **CTA9**, as trithiocarbonate anions are very potent nucleophiles that are efficiently alkylated by bromides as well as by chlorides. ^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 1.59 (d, 3H, $\underline{H}_3$C-CHCl-), 1.75 (d, 3H, $\underline{H}_3$C-CHBr-), 2.99 (d + d, 6H, -N(C$\underline{H}_3$)$_2$), 4.51-4.59 (m, 1H, -C$\underline{H}$Br(CH$_3$)-, -C$\underline{H}$Cl(CH$_3$)-). ^{13}C-NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 20.8 (-CHCl(C$\underline{H}_3$), 21.5 (-CHBr(C$\underline{H}_3$)-), 36.0, 37.1 (-N(C$\underline{H}_3$)$_2$, Cl-product), 36.1, 37.3 (-N(C$\underline{H}_3$)$_2$, Br-product), 38.2 (-C$\underline{H}$Br(CH$_3$)-), 49.3 (-C$\underline{H}$Cl(CH$_3$)-), 168.7 (-C(=O)-O-, Cl-product)168.9 (-C(=O)-O-, Br-product).

(ii) Coupling to N,N-dimethyl 2-(butylsulfanylthiocarbonylsulfanyl) propionamide. Under nitrogen flow, a 50 wt% aqueous solution of NaOH (3.11 g, 38.9 mmol) was added dropwise to 1-butanethiol (3.50 g, 38.9 mmol) dissolved in 20 mL THF. The dropwise addition of CS_2 (2.96 g, 40 mmol) gave a clear, bright yellow solution. 7.00 g (41.5 mmol) of the mixture of *N,N*-dimethyl 2-bromopropionamide and *N,N*-dimethyl 2-chloropropionamide (3:1 mole/mole) were added dropwise. White flakes of sodium halide precipitated after a while. The reaction mixture was stirred at ambient temperature over night. 50 mL of water were added and the mixture was extracted twice with 50 mL of hexane. The combined hexane phases were washed with water and dried over anhydrous $MgSO_4$. The solvent was evaporated. Under cooling to 4°C, the product crystallized as bright yellow needles. Yield: 9.7 g (94%). The product was pure according to ^{1}H NMR spectroscopy. Prior to the investigations of the UV-vis characteristics, the product was recrystallized from *n*-hexane. m.p. 32°C. Elemental analysis ($C_{10}H_{19}NOS_3$, M_r = 265.46): Calc: C 45.25, H 7.21, N 5.28, S 36.24 Found: C 45.28, H 7.29, N 5.25, S 36.53. MS (EI, negative ions): m/z = 265. ^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 0.93 (t, 3H, C$\underline{H}_3$-CH$_2$-),

1.42 (m, 2H, -S-C-C-C$\underline{H}_2$-), 1.55 (d, 3H, -S-CH(C$\underline{H}_3$)-), 1.68 (m, 2H, -S-C-C$\underline{H}_2$-), 3.02 (s + s, 6H, -N(C$\underline{H}_3$)$_2$), 3.36 (t, 2H, -S-C$\underline{H}_2$-), 5.18 (q, 1H, -S-C$\underline{H}$(CH$_3$)-). ^{13}C-NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 13.6 ($\underline{C}H_3$-CH$_2$-), 17.6 (-S-CH($\underline{C}H_3$)-), 22.0 (-S-C-C-$\underline{C}H_2$-), 29.9 (-S-C-$\underline{C}H_2$-), 36.1 (-N($\underline{C}H_3$)$_2$), 36.9 (-S-$\underline{C}H_2$-), 37.4 (-N($\underline{C}H_3$)$_2$), 46.3 (-S-$\underline{C}$H(CH$_3$)-), 170.2 (-C(=O)-N), 223.1 (-S-C(=S)-S-). FT-IR (KBr, selected bands, wavenumber in cm^{-1}): 2951, 2928, 2868, 1647, 1491, 1460, 1389, 1081, 1039, 825, 729.

2-(butylsulfanylthiocarbonylsulfanyl)-2-methyl propionic acid (CTA10).

The title compound was synthesized adapting a procedure by Lai et al.[4] m.p. 52°C. Elemental analysis ($C_9H_{16}O_2S_3$, M_r = 252.42): Calc: C 42.82, H 6.39, S 38.11, Found: C 42.79, H 6.64, S 38.17. MS (EI, negative ions): m/z = 252. ^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 0.93 (t, 3H, C$\underline{H}_3$-CH$_2$-), 1.42 (m, 2H, -S-C-C-C$\underline{H}_2$-), 1.67 (m, 2H, -S-C-C$\underline{H}_2$-), 1.72 (s, 6H, -S-C(C$\underline{H}_3$)$_2$-), 3.29 (t, 2H, -S-C$\underline{H}_2$-). ^{13}C-NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 13.6 ($\underline{C}H_3$-CH$_2$-), 22.1 (-S-C-C-$\underline{C}H_2$-), 25.2 (-S-C($\underline{C}H_3$)$_2$-), 29.9 (-S-C-$\underline{C}H_2$-), 36.7 (-S-$\underline{C}H_2$-), 55.6 (-S-$\underline{C}$(CH$_3$)$_2$-), 178.7 (-COOH), 220.8 (-S-C(=S)-S-). FT-IR (KBr, selected bands, wavenumber in cm^{-1}): 2949, 2924, 2870, 2656, 2551, 1693, 1462, 1419, 1284, 1086, 1049, 916, 816.

Methyl 2-(butylsulfanylthiocarbonylsulfanyl)-2-methyl propionate (CTA11).

CTA10 was dissolved in CH_2Cl_2 and transferred to a separatory funnel containing purified water. NaOH (0.1 M) was added in understochiometric amounts to deprotonate the acid but to avoid hydrolysis of the trithiocarbonate. The sodium salt formed was extracted into the water phase and the aqueous solution was separated and lyophilized. This salt (2.5 g, 9.1 mmol) was dissolved in 10 mL of anhydrous DMF and transferred to a 25-mL round bottom flask. Dimethylsulfate (3.5 g, 27.8 mmol) was added dropwise under stirring at ambient temperature. Afterwards, the mixture was stirred for 1.5 h at ambient temperature, and for 19 h at 30°C. Water (20 mL) was added to the reaction mixture and the product was extracted with 100 mL of hexane. The organic phase was washed with 5 wt% aqueous $NaHCO_3$ and brine. After drying over anhydrous $MgSO_4$, the solvent was evaporated and the raw product was obtained as deep yellow oil (2.5 g). TLC (eluent: *n*-hexane) of the crude product disclosed three side products. Purification by column chromatography (silicagel 60, Merck, 0.040-0.063 mm, eluent: *n*-hexane) gave the pure product as an orange liquid (1.2 g, 48%). Elemental analysis ($C_{10}H_{18}O_2S_3$, M_r = 266.44): Calc: C 45.08, H 6.81, S 36.10. Found: C 44.81, H 6.99 S 35.93. MS (EI, negative ions): m/z = 266. ^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 0.92 (t, 3H, C$\underline{H}_3$-CH$_2$-), 1.40 (m, 2H, -S-C-C-C$\underline{H}_2$-), 1.65 (m, 2H, -S-C-C$\underline{H}_2$-), 1.68 (s, 6H, -S-C(C$\underline{H}_3$)$_2$-), 3.28 (t, 2H, -S-C$\underline{H}_2$-), 3.70 (s, 3H, -O-C$\underline{H}_3$). ^{13}C-NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 13.6 ($\underline{C}H_3$-CH$_2$-), 22.1 (-S-C-C-$\underline{C}H_2$-), 25.3 (-S-C($\underline{C}H_3$)$_2$-), 29.9 (-S-C-$\underline{C}H_2$-), 36.6 (-S-$\underline{C}H_2$-), 53.0 (-O-$\underline{C}H_3$),

55.8 (-S-C(CH$_3$)$_2$-), 173.5 (-C(=O)-O-), 221.5 (-S-C(=S)-S-). FT-IR (KBr, selected bands, wavenumber in cm^{-1}): 2956, 2930, 2872, 1733, 1463, 1432, 1382, 1260, 1152, 1125, 1055, 813.

1,4-bis(octadecyl trithiocarbonato methyl) benzene (CTA15).

Under nitrogen flow, a 16 wt% aqueous NaOH solution (10.0 g, 40 mmol) was added dropwise at ambient temperature to a vigorously stirred solution of 1-octadecanethiol (11.5 g, 40 mmol) in THF (20 mL). The thiolate precipitated as white solid. Then, CS_2 (3.1 g, 40 mmol) was added dropwise at ambient temperature and a clear, intensely yellow solution was obtained. 1,4-bis(chloromethyl) benzene (3.5 g, 20 mmol) dissolved in 20 mL of THF were added slowly to the reaction mixture. Upon addition of the halide, the product precipitated and the reaction mixture turned into a thick paste. To improve mixing of reagents, 80 mL of THF were added. The mixture was stirred over night at 45°C. The precipitated solid was filtered off and washed several times with THF. The raw product was dissolved in $CHCl_3$ and dried over anhydrous $MgSO_4$. The solution was concentrated under slight heating and then left at ambient temperature to crystallize. A bright yellow, solid product (7.5 g, 45%) was obtained. Elemental analysis ($C_{46}H_{82}S_6$, M_r = 827.53): Calc: C 66.76, H 9.99, S 23.25. Found: C 66.63, H 10.46, S 23.36. ^{1}H NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 0.88 (t, 6H, -C<u>H</u>$_3$), 1.06-1.46 (m, 60H, -C(2)<u>H</u>$_2$ - C(16)<u>H</u>$_2$-), 1.65-1.75 (m, 4H, -S-C-C<u>H</u>$_2$-), 3.36 (t, 4H, -S-C<u>H</u>$_2$-), 4.58 (s, -CH$_2$-aryl), 7.28 (s, 4H, aryl). ^{13}C NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 14.1 (-<u>C</u>H$_3$), 22.7 (-<u>C</u>H$_2$-CH$_3$), 28.0, 28.8, 29.1, 293, 29.4, 29.5, 29.7 (methylene), 31.9 (-S-C-<u>C</u>H$_2$-), 37.1 (-S-<u>C</u>H$_2$-), 40.9 (-<u>C</u>H$_2$-aryl), 129.5 (<u>C</u>H aryl), 134.8 (<u>C</u> aryl), 223.6 (-S-C(=S)-S-). FT-IR (KBr, selected bands, wavenumber in cm^{-1}): 2955, 2916, 2850, 1472, 1074, 1063, 837, 822, 719.

4-Butylsulfanylthiocarbonylsulfanylmethyl-benzoic acid (CTA17)

A solution of 40 mL 1,2-dimethoxyethane, potassium hydroxide (1.5 g, 26.7 mmol) and 1-butanethiol (1.3 g, 14.4 mmol) was stirred under nitrogen flow at 60º C for 40 min, before 1.0 mL (16.6 mmol, d = 1.262 g/mL) of carbon disulphide were added dropwise and the reaction allowed to proceed for an additional 15 min. To the bright yellow solution 3.0 g (13.9 mmol) of 4-bromomethylbenzoic acid, dissolved in 40 mL of 1,2-dimethoxyethane were added and the mixture stirred for 2 h at 60º C, then left over night at room temperature. After the completion of the reaction, the organic phase was mixed with 150 mL of 0.1 M HCl solution. The precipitated solid was filtered off and washed several times with water. Recrystallisation from n-hexane/THF: 4/1 afforded a bright yellow crystalline product. Yield: 2.6 g (62 %). Elemental analysis ($C_{13}H_{16}O_2S_3$ M_w = 300.46): Calc.: C 51.97, H 5.37, S 32.02 Found: C 51.88, H 5.22, S 31.76 MS (EI, negative ions): m/z = 300. ^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 0.94 (t, 3H, <u>CH$_3$</u>-CH$_2$-), 1.38-1.50 (m, 2H, CH$_3$-<u>CH$_2$</u>-CH$_2$-), 1.74-1.64 (m, 2H, CH$_3$-CH$_2$-<u>CH$_2$</u>-), 3.40 (t, 2H, -S-<u>CH$_2$</u>-CH$_2$), 4.67 (s, 2H, -S-CH$_2$-aryl), 7.44 (d, 2H, aryl), 8.05 (d, 2H, aryl). ^{13}C-NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 13.6 (<u>CH$_3$</u>-CH$_2$-), 22.0 (CH$_3$-<u>CH$_2$</u>-CH$_2$-), 30.0 (CH$_3$-CH$_2$-<u>CH$_2$</u>-), 37.0 (-S-<u>CH$_2$</u>-

CH_2), 40.5 (-S-$\underline{CH_2}$-aryl), 128.6 (-S-CH_2-$\underline{C}$ aryl), 129.3 (CH aryl), 130.5 (CH aryl), 141.8 (COOH-$\underline{C}$ aryl), 171.7 (COOH).

1,2 bis (4-(*t*-butoxycarbonyl)benzyl sulfanylthiocarbonyl sulfanyl) ethane (CTA18)

(i) tert-butyl 4-methylbenzoate. Adapting a literature procedure,[5] concentrated sulfuric acid (7.8 mL, 148 mmol) was added to a vigorously stirred suspension of anhydrous magnesium sulfate (73.0 g, 606 mmol) in 400 mL of dry dichloromethane. The mixture was stirred for 15 minutes, after which the 4-methylbenzoic acid (20.2 g, 148 rnmol) was added. *Tert*-butanol (70 mL, 746 mmol) was added last. The mixture was stoppered tightly in a pressure resistant flask and stirred at room temperature. After 19 h, the reaction vessel was cooled in a dry/ice isopropanol bath to reduce any pressure that might have been generated during the reaction. The content was poured into 1 L of saturated sodium bicarbonate solution and stirred until all magnesium sulfate had dissolved. The organic phase was separated, washed with brine, dried with $MgSO_4$ and concentrated to afford the crude t-butyl ester which was purified by distillation in a Kugelrohr apparatus (110º C, 2 mbar) to give a colourless oil. Yield: 20.4g (72 %) ^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 1.59 (s, 9H, $(CH_3)_3$-C-), 2.39 (s, 3H, CH_3-aryl), 7.21 (d, 2H, 2H-aryl), 7.88 (d, 2H, 2H-aryl).

(ii) tert-butyl 4-(bromomethyl) benzoate. A suspension of the previously synthesised *tert*-butyl 4-methylbenzoate (20.0 g, 0.104 mol), N-bromosuccinimide (18.9 g, 0.106 mol), and azobisisobutyronitrile (0.068 g, 0.417 mmol) in CCl_4 (140 mL) was heated to 95ºC. After the beginning of the reaction, indicated by a strong boiling, the mixture was allowed to reflux for 1 h. The suspension was cooled to room temperature and the precipitated N-succinimide filtered. The organic layer was washed with saturated aqueous $NaHCO_3$ solution (2 x 75 mL) and distilled water (1 x 75 mL), dried over anhydrous $MgSO_4$, filtered and evaporated to give a slightly yellow oil. The oil crystallised at room temperature to form a white solid. TLC analysis (Silica, hexane/toluene: 3/1) indicated the presence of 4-methylbenzoic acid *tert*-butyl ester, confirmed by ^{1}H-NMR. From the signal integration, the crude product contains 86.4 mol% of *tert*-butyl 4-(bromomethyl) benzoate, 8.8 mol% of *tert*-butyl 4-methylbenzoate of and 4.8 mol% of *tert*-butyl 4-(dibromomethyl) benzoate. It was used without further purification for the synthesis of CTA18. Yield: crude 20.4 g (corrected 62 %) ^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 1.59 (s, 9H, $(CH_3)_3$-C-), 4.49 (s, 2H, Br-CH_2-aryl), 7.43 (d, 2H, 2H-aryl), 7.96 (d, 2H, 2H-aryl).

(iii) 1,2 bis (4-(t-butoxycarbonyl)benzyl sulfanylthiocarbonyl sulfanyl) ethane. 6 mL deionised water, potassium hydroxide (0.88 g, 15.7 mmol), Aliquat® 336 (0.44 g, 1.1 mmol) and 1,2-ethandithiol (0.45 mL, 6.6 mmol, d = 1.123 g/mL) were stirred at room temperature for 30 min, before 1.0 mL (16.5 mmol, d = 1.262 m/mL) of carbon disulphide was added dropwise. The reaction was allowed to proceed for an additional 90min. 4-bromomethylbenzoic acid *tert*-butyl ester, dissolved in 18 mL benzene were added to the bright yellow solution 4.0 g of the crude (corresponding to pure 13.6 mmol), and the

mixture stirred over night at room temperature. The organic layer turned progressively orange and the aqueous phase became colourless. After the completion of the reaction the benzene layer was washed with three portions of 25 mL water, dried on $MgSO_4$ and evaporated. The solid product was recrystallised from THF/hexane to give bright yellow crystals. Yield: 3.8 g (86%). Elemental analysis: ($C_{13}H_{16}O_2S_3$ M_w = 626.96) Calculated: C 53.64, H 5.47, S 30.69 Found: C 53.72, H 5.18, S 30.48 MS (EI, negative ions): m/z = 626. ^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 1.58 (s, 9H, $(CH_3)_3$-C-), 3.69 (s, 2H, S-CH_2-aryl), 4.63 (s, 2H, -S-CH_2-CH_2-S-), 7.37 (d, 2H, 2H-aryl), 7.93 (d, 2H, 2H-aryl). ^{13}C-NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 28.1 (($\underline{CH_3}$)$_3$-C-), 34.8 (-S-$\underline{CH_2}$-$\underline{CH_2}$-S-), 41.0 (S-$\underline{CH_2}$-aryl), 81.1 ((CH_3)$_3$-$\underline{C}$-), 129.0 (COOtBu-$\underline{C}$ aryl), 129.8 (CH aryl), 131.5 (CH aryl), 139.6 (-S-CH_2-$\underline{C}$ aryl), 165.2 ($\underline{C}$OOtBu-C aryl).

Butyl-1-phenylethyltrithiocarbonate (CTA19)

Triethylamine (5.4 g, 31.6 mmol) and 1-butanethiol (1.9 mL, 17.7 mmol, d = 0.84 g/mL) were stirred with 15 mL of chloroform at room temperature for 30 min, before 2.7 mL (44.8 mmol, d = 1.262 g/mL) of carbon disulphide were added dropwise. After an additional 15 min, 2.2 mL (15.5 mmol, d = 1.356 g/mL) of (1-bromoethyl)benzene were slowly added. The mixture was stirred over night. The organic phase was washed with four portions of 15 mL deionised water, dried over $MgSO_4$,evaporated and dried in high vacuo to yield a deep orange oil. Yield: 3.9 g (89 %). Elemental analysis: ($C_{13}H_{18}S_3$ M_w = 270.48): Calculated: C 57.73, H 6.71, S 35.56 Found: C 57.67, H 6.53, S 35.15 MS (EI, negative ions): m/z = 270. ^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 0.94 (t, 3H, $\underline{CH_3}$-CH_2-), 1.43 (sext, 2H, CH_3-$\underline{CH_2}$-CH_2-), 1.68 (quint, 2H, CH_3-CH_2-$\underline{CH_2}$-), 1.77 (d, 3H, -S-CH-$\underline{CH_3}$), 3.35 (t, 2H, -S-$\underline{CH_2}$-CH_2-), 5.36 (q, 1H, -S-$\underline{CH}$-CH_3), 7.24-7.41 (m, 5H, aryl). ^{13}C-NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 13.5 ($\underline{CH_3}$-CH_2-), 21.3 (-S-CH-$\underline{CH_3}$), 22.0 (CH_3-$\underline{CH_2}$-CH_2-), 30.0 (CH_3-CH_2-$\underline{CH_2}$-), 36.5 (-S-$\underline{CH_2}$-CH_2), 50.0 (-S-$\underline{CH}$-CH_3), 127.60 (CH aryl para), 127.63 (CH aryl ortho), 128.6 (CH aryl metha), 141.1 (CH-$\underline{C}$ aryl).

S-butyl-S'-naphth-2-ylmethyl trithiocarbonate (CTA20).

Under nitrogen flow, a 50 wt% aqueous solution of NaOH (3.35 g, 42 mmol) was added dropwise to 1-butanethiol (3.7 g, 41 mmol) dissolved in 20 mL of THF. CS_2 (3.04 g, 40 mmol) was added dropwise at ambient temperature to the white suspension of precipitated thiolate and a clear, bright yellow solution formed. After stirring for 10 min, 2-bromomethyl naphthalene (8.8 g, 39.8 mmol) dissolved in 20 mL of THF was added. The reaction mixture was stirred over night at ambient temperature. Then, 100 mL of water were added and the solution was extracted with *n*-hexane. The hexane phase was washed with brine and dried over anhydrous $MgSO_4$. The concentrated organic phase was left at -20°C, and the product crystallized as bright, light yellow needles and was pure according to ^{1}H and ^{13}C NMR spectroscopy. Yield: 8.36 g (67%). Elemental analysis ($C_{16}H_{18}S_3$, M_r = 306.51): Calc: C 62.70 H 5.92 S 31.38, Found: C 62.70, H 6.03, S 31.74. MS (EI, negative ions): m/z = 306. ^{1}H-NMR (300 MHz in

$CDCl_3$, δ in ppm): δ = 0.95 (t, 3H, C<u>H</u>$_3$-), 1.45 (m, 2H, -S-C-C-C<u>H</u>$_2$-), 1.70 (m, 2H, -S-C-C<u>H</u>$_2$-), 3.40 (t, 2H, -S-C<u>H</u>$_2$-), 4.79 (s, 2H, -C<u>H</u>$_2$-aryl), 7.42-7.51 (m, 3H, naphthyl), 7.79-7.83 (m, 4H, naphthyl). ^{13}C-NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 13.6 (<u>C</u>H$_3$-), 22.1 (-S-C-C-<u>C</u>H$_2$-), 30.0 (-S-C-<u>C</u>H$_2$-), 36.8 (-S-<u>C</u>H$_2$-), 41.6 (-<u>C</u>H$_2$-naphthyl), 126.3, 127.0, 127.7, 128.2, 128.5 (<u>C</u>H naphthyl), 132.6, 132.8, 133.3 (C naphthyl), 223.7 (-S-C(=S)-S-). FT-IR (KBr, selected bands, wavenumber in cm^{-1}): 2956, 2924, 2856, 1419, 1229, 1192, 1088, 1053, 812, 758.

S-butyl-S'-acridin-4-ylmethyl trithiocarbonate (CTA21).

In a 100 mL sealed three-neck flask, 1-butanethiol (207.2 mg, 2.3 mmol) butanethiol and triethylamine (283.3 mg, 2.8 mmol) were mixed under N_2. The solution was cooled to 0°C and CS_2 (196.3 mg, 2.8 mmol) was added slowly. After 30 min, 4-bromomethyl acridine (520 mg, 1.91 mmol) dissolved in 10 mL of $CHCl_3$ was added, and the reaction was allowed to proceed overnight. After washing with water and extracting the organic materials from the reaction mixture by CH_2Cl_2, the combined organic phases were dried over anhydrous Na_2SO_4. The solution was filtered, the filtrate concentrated *in vacuo*, and the remaining homogeneous residue was purified by column chromatography (eluent hexane/CH_2Cl_2 (2/1 v/v, R_f = 0.44) to afford **CTA21** (550 mg, 80%) as a yellow oil. Elemental analysis ($C_{19}H_{19}NS_3$, M_r = 357.56): Calc: C 63.82, H 5.36, N 3.92, S 26.90; Found: C 63.69, H 5.01, N 3.92, S 27.02. MS-EI: *m/Z* = 357 [M^+]. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.33 Hz, 3 H, CH_3), 1.42 (sext, *J* = 7.33 Hz, 2 H, CH_2), 1.68 (m, 2 H, CH_2), 3.39 (t, *J* = 7.33 Hz, 2 H, CH_2), 5.46 (s, 2 H, CH_2), 7.42 (dd, *J* = 6.82, 8.51 Hz, 1 H), 7.52 (ddd, *J* = 1.03, 6.64, 8.09 Hz, 1 H), 7.76 (ddd, 1.40, 6.62, 8.12 Hz, 1 H), 7.87-7.97 (m, 3 H), 8.26 (d, *J* = 8.78 Hz, 1 H), 8.68 (s, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.5 (q, CH_3), 22.0, 30.1, 36.7, 37.3 (4 t, 4 CH_2), 125.2, 125.8 (2 d, acridine 2 CH), 126.4, 126.5 (2 s, acridine 2 C), 127.9, 128.2, 130.1, 130.4 (4 d, acridine 4 CH), 134.5 (s, acridine C), 135.9 (d, acridine CH), 147.1, 148.4 (2 d, acridine 2 CH), 225.3 (s, -S-C=(S)S-). FT-IR (KBr, selected bands, in cm^{-1}): $\tilde{\nu}$ = 2955, 2925 (CH aryl), 1616, 1522, 1462, 1403 (C=C, C=N aryl), 1050, 1029 (C=S), 900, 852, 809, 770, 735 (CH aryl).

4,5-bis(butyl trithiocarbonato methyl) acridine (CTA22).

In a 100 mL sealed three-neck flask, 1-butanethiol (397.4 mg, 4.3 mmol) and triethylamine (495.8 mg, 4.9 mmol) of were added under N_2. The solution was cooled at 0 °C and CS_2 (343.6 mg, 4.9 mmol) was added slowly. After 30 min, the mixture was treated bis(bromomethyl)acridine with (720 mg, 1.97 mmol) dissolved in 10 mL $CHCl_3$, and the reaction was allowed to proceed overnight. The mixture was washed with water and extracted with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated *in vacuo*. The homogeneous residue was purified by column chromatography (eluent hexane/CH_2Cl_2 9/1 v/v, R_f = 0.18) to afford the title compound (1.05

g, 99%) as a yellow solid (m.p. 68-70°C). Elemental analysis ($C_{25}H_{29}NS_6$, M_r = 535.89): Calc: C 56.03, H 5.45, N 2.61, S 35.90; Found: C 55.69, H 5.38, N 2.57, S 35.37. MS-EI: *m/Z* = 535 [M^+]. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.4 Hz, 6 H, 2 CH_3), 1.42 (sext, *J* = 7.4 Hz, 4 H, 2 CH_2), 1.68 (quint, *J* = 7.4 Hz, 4 H, 2 CH_2), 3.39 (t, *J* = 7.4 Hz, 2 H, 2 CH_2), 5.43 (s, 4 H, 2 CH_2), 7.47 (dd, *J* = 6.8, 8.5 Hz, 2 H, acridine CH), 7.91-7.95 (m, 4 H, acridine 4 CH), 8.73 (s, 1 H, acridine CH). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.6 (q, CH_3), 22.1, 30.1, 36.7, 37.7 (4 t, 4 CH_2), 125.6 (d, acridine CH), 126.6 (s, acridine C), 128.1, 130.9 (2 d, acridine 2 CH), 134.6 (s, acridine C), 136.5 (d, acridine CH), 146.2 (s, acridine C), 225.1 (s, -S-C=(S)S-). FT-IR (KBr, selected bands, in cm^{-1}): $\tilde{\nu}$ = 2952, 2932, 2867 (CH aryl), 1529, 1456, 1423, 1380 (C=C, C=N aryl), 1060 1039, 1030, 1014 (C=S), 898, 879, 815, 753 (CH aryl).

Monomer Synthesis.

Methoxy diethylene glycol acrylate (MDEGA)

Diethylene glycol monomethyl ether (40.0 g, 0.33 mol), triethylamine (37.0 g, 0.37 mol) and 250 mL of dry dichloromethane were added to a 1L three-necked flask, placed in an isopropanol/dry ice bath and purged with N_2 for 30 min. Acryloyl chloride (30.0 mL, 0.37 mol) and hydroquinone (0.3 g, 27 mmol) dissolved in 190 mL of dichloromethane were added dropwise under nitrogen atmosphere. The reaction was maintained in the ice bath for 1h, and then left overnight at room temperature. The precipitated ammonium salt was filtered off, the organic phase washed two times with 250 mL of saturated sodium bicarbonate solution and two times with 250 mL of deionised water. The collected organic phase was dried over $MgSO_4$ and concentrated by rotary evaporation at ambient temperature to give an orange viscous liquid. Further distillation in Kugelrohr apparatus (p < 1 mbar, 85-100°C) gave a colourless viscous liquid. Yield: 43.1 g, 75 %.

^{1}H-NMR (300 MHz in $CDCl_3$, δ in ppm): δ = 3.36 (s, 3H, $\underline{CH_3}$-O-), 3.52-3.55 (m, 2H, CH_3-O-$\underline{CH_2}$-), 3.62-3.65 (m, 2H, O-CH_2-$\underline{CH_2}$-O-), 3.72 (t, 2H, -CH_2-O-$\underline{CH_2}$-CH_2-), 4.30 (t, 2H, -CH_2-O-CH_2-$\underline{CH_2}$-O-), 5.82 (dd, 1H, $\underline{CH_2}$=CH-COO-), 6.13 (dd, 1H, CH_2=$\underline{CH}$-COO-), 6.41 (dd, 1H, $\underline{CH_2}$=CH-COO-)

^{13}C-NMR (75 MHz in $CDCl_3$, δ in ppm): δ = 58.9 ($\underline{CH_3}$-O-), 63.5 (-CH_2-O-CH_2-$\underline{CH_2}$-O-), 69.0 (-CH_2-O-$\underline{CH_2}$-CH_2-), 70.4 (-O-CH_2-$\underline{CH_2}$-O-), 71.8 (CH_3-O-$\underline{CH_2}$-), 128.2 (CH_2=$\underline{CH}$-COO-), 130.7 ($\underline{CH_2}$=CH-COO-), 166.0 (-CH-$\underline{C}$OO-CH_2-).

Polymer Synthesis.

Polystyrene

In a typical procedure, styrene (11.0 mL, 96 mmol, d = 0.916) and CTA18 (1.5 g, 2.4 mmol) were

mixed in a round bottom flask. The flask was sealed with a rubber septum and purged with nitrogen for 15 min. The polymerisation took place for 18h at 110°C. The obtained yellow viscous liquid was diluted with acetone and precipitated 3 times in methanol. The collected polymer was dried in vacuo at room temperature over 48 h to give 5.1 g of yellow powder.

Poly(methoxy diethylene glycol acrylate)

In a typical procedure, methoxy diethylene glycol acrylate (2.3 g, 13 mmol), CTA 18 (0.0596 g, 0.095 mmol) and AIBN (0.0023g, 0.014 mmol) were mixed and purged with N_2 for 15 min at room temperature. After 4 h at 70°C, the polymerisation was quenched by placing the flask into liquid nitrogen. The obtained yellow liquid was precipitated three times in *n*-hexane, and dried in vacuo at room temperature over 48h to give a 1.7 g (71 %) of a highly viscous yellow oil.

References:

1. T. P. T. Le, G. Moad, E. Rizzardo and S. H. Thang, 1998.
2. W. Thiel, J. Fabian and B. Friebe, *J. Prakt. Chem.*, 1986, **328**, 812-823.
3. J. T. Rademacher, M. Baum, M. E. Pallack, W. J. Brittain and J. William J. Simonsick, *Macromolecules*, 2000, **33**, 284-288.
4. J. T. Lai, D. Filla and R. Shea, *Macromolecules*, 2002, **35**, 6754-6756.
5. S. W. Wright, D. L. Hageman, A. S. Wright and L. D. McClure, *Tetrahedr. Lett.*, 1997, **38**, 7345-7348.