Supporting Information

The Application of a Photochromic Probe to Monitor the Self-Assembly of Thermosensitive Block Copolymers.

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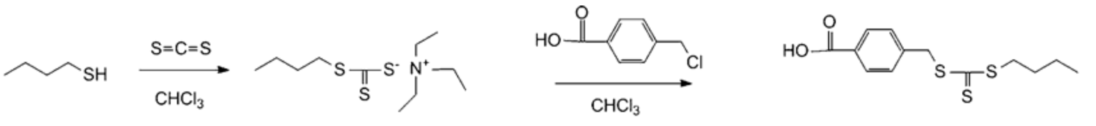
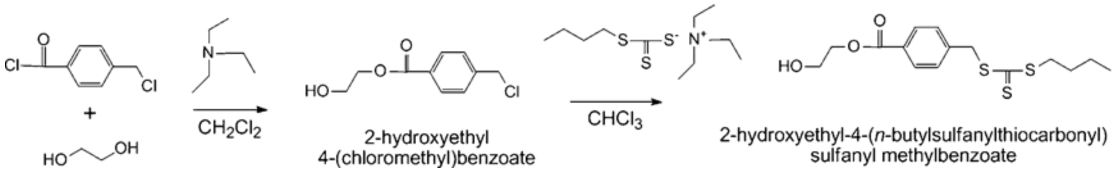
(1) Synthesis of RAFT Agents and SOX derivatives



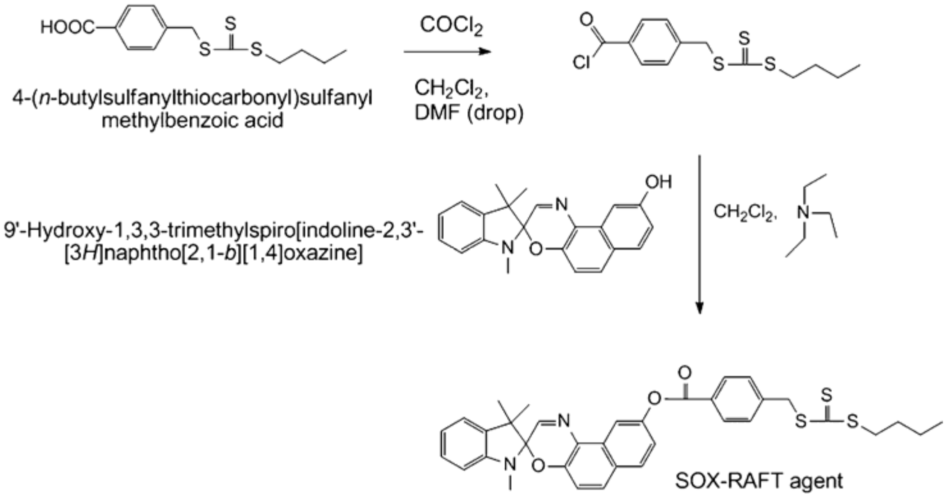
4-(*n*-butylsulfanylthiocarbonyl)sulfanyl
methylbenzoic acid

4-(*n*-Butylsulfanylthiocarbonyl)sulfanyl methylbenzoic acid, RAFT agent. To a stirring solution of 1,4 butanethiol (0.035 mol, 3.40 g), carbon disulfide (0.070 mol, 5.30 g) in chloroform (50 mL) was added triethylamine (0.116 mol, 11.74 g) dropwise. The solution became yellow and then orange on formation of triethylammonium trithiocarbonate salt. The solution was left to stir at room temperature for 2 hours and then 4-chloromethyl benzoic acid (0.029 mol, 5 g), also dissolved in chloroform (30 mL) was added dropwise. The solution was left to stir for 16 hours at room temperature. It was then washed 5 × with 0.1 M HCl, the organic layers combined, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum and the remaining yellow RAFT agent, 4-(*n*-butylsulfanylthiocarbonyl)sulfanyl methylbenzoic acid, was collected by filtration with hexane (7 g, 80%). ^{1}H NMR (400 MHz, d_6-acetone) δ: 0.92 (t, 3H, *J* 7.3 Hz, CH_3), 1.39 - 1.49 (m, 2H, CH_2), 1.66 - 1.73 (m, 2H, CH_2), 3.44 (t, *J* 7.3 Hz, 2H, SCH_2), 4.78 (s, 2H, $ArCH_2$), 7.55 (d, *J* 8.4 Hz, 2H, ArH), 8.01 (d, *J* 8.4 Hz, 2H, ArH) ppm. ^{13}C NMR (100 MHz, d_6-acetone) δ: 13.8, 22.6, 30.8, 37.3, 40.9, 130.2, 130.7, 130.7, 142.0, 167.2, 224.5 ppm.



2-Hydroxyethyl-4-(*n*-butylsulfanylthiocarbonyl)sulfanyl methyl benzoate, RAFT agent. To an ice-cooled solution of dried ethylene glycol (18.0 g, 0.290 mol) and triethylamine (6.1 mL, 4.43 g, 0.044 mol) in dry dichloromethane (30 mL) was added dropwise, 4-(chloromethyl)benzoyl chloride (5.5 g, 0.029 mol) under argon. The solution was stirred with ice cooling for half an hour and was then left to stir for an additional 12 hours at room temperature. The solution was washed with water 3 × and then brine. The organic layer was dried with anhydrous MgSO$_4$ and the solvent was evaporated under vacuum to give 2-hydroxyethyl 4-(chloromethyl)benzoate, a thick yellow oil that became a wax on standing (6.41 g). ^{1}H NMR showed this intermediate product to be of sufficient purity for subsequent use.

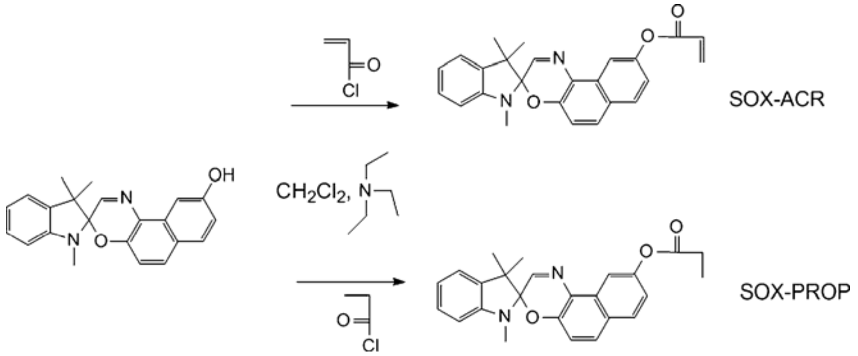
The same procedure as described above was followed for the synthesis of the corresponding triethylammonium trithiocarbonate salt in chloroform, using 1,4 butanethiol (0.038 mol, 3.45 g), carbon disulfide (0.071 mol, 5.36 g) and triethylamine (8.91 g, 0.0.088 mol). 2-Hydroxyethyl 4-(chloromethyl)benzoate (0.029 mol, 6.31 g), dissolved in chloroform was then added dropwise and the solution left to stir at room temperature for 16 hours. The chloroform was removed under vacuum and the residue dissolved in diethyl ether. It was then washed with water and dried with anhydrous MgSO4. The solvent was then removed under vacuum and the remaining yellow oil was purified by column chromatography (silica gel, diethyl ether/hexane, 3:1) to give the RAFT agent, 2-hydroxyethyl-4-(*n*-butylsulfanylthiocarbonyl)sulfanyl methylbenzoate, as a waxy yellow solid (3.3 g, 30%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.94 (t, 3H, *J* 7.3 Hz, CH$_3$), 1.39 - 1.49 (m, 2H, CH$_2$), 1.66 - 1.73 (m, 2H, CH$_2$), 3.39 (t, *J* 7.3 Hz, 2H, SCH$_2$), 4.67 (s, 2H, ArCH$_2$), 7.45 (d, *J* 7.7 Hz, 2H, ArH), 8.05 (d, *J* 7.3 Hz, 2H, ArH) ppm. ^{13}C NMR (100 MHz, d_6-acetone) δ: 14.8, 23.6, 38.3; 41,8, 31.8, 61.7, 68.5, 131.2, 131.5, 131.6, 143.1, 167.4, 225.5 ppm.



9'-(4-((*n*-Butylsulfanylthiocarbonyl)sulfanyl)methylbenzoyl)-1,3,3-trimethylspiro[indoline-2,3'-[3*H*]naphtho[2,1-*b*][1,4]oxazine], SOX-RAFT agent.

4-(*n*-butylsulfanylthiocarbonyl)sulfanyl methylbenzoic acid (2.0 g, *ca.* 6.66 mmol) was dissolved in dry CH_2Cl_2 (100 mL) under nitrogen and 1 small drop DMF added. To the mixture was added oxalyl chloride (1.52 g, 1.03 mL, 11.98 mmol) using a gas-tight syringe. The mixture was stirred at ambient temperature for 3 hours. The solvent and excess reagents were removed under vacuum with residual traces of oxalyl chloride removed with the aid of 1,2-dichloroethane. Analysis by ^{1}H NMR showed quantitative conversion to the corresponding 4-(*n*-butylsulfanylthiocarbonyl)sulfanylmethylbenzoyl chloride. ^{1}H NMR (400 MHz, d_6-acetone) δ: 0.92 (t, 3H, *J* 7.3 Hz, CH_3), 1.38 - 1.47 (m, 2H, CH_2), 1.65 - 1.72 (m, 2H, CH_2), 3.42 (t, *J* 7.3 Hz, 2H, SCH_2), 4.82 (s, 2H, $ArCH_2$), 7.66 (d, *J* 8.42 Hz, 2H, ArH), 8.09 (d, *J* 8.42 Hz, 2H, ArH) ppm. ^{13}C NMR (100 MHz, d_6-acetone) δ: 13.8, 22.6, 30.8, 37.5, 40.4, 130.9, 132.4, 132.8, 145.8, 168.1, 224.2 ppm.

To an ice-cooled solution of 9'-hydroxy-1,3,3-trimethylspiro[indoline-2,3'-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (see Kakishita et al. *J. Heterocyclic Chem.* 1992, 29, 1709) (2.09 g, 6.05 mmol) and triethylamine (1.35 g, 1.86 mL, 13.32 mmol) in dry CH_2Cl_2 (100 mL), was added dropwise the full quantity of 4-(*n*-butylsulfanylthiocarbonyl)sulfanylmethylbenzoyl chloride in dry CH_2Cl_2 (35 mL). The mixture was left to stir at room temperature overnight. The solvent was then removed under vacuum and the residue purified by column chromatography (silica gel, diethyl ether/hexane, 3:2) to give the title compound as mustard coloured solid (3.5 g, 92%). ^{1}H NMR (400 MHz, d_6-acetone) δ: 0.94 (t, 3H, *J* 7.3 Hz, CH_3), 1.35 (2 × overlapping s, 6H, 2 × CH_3), 1.41 - 1.50 (m, 2H, CH_2), 1.67 - 1.73 (m, 2H, CH_2), 2.78 (s, 3H, N-CH_3), 3.46 (t, *J* 7.3 Hz, 2H, SCH_2), 4.85 (s, 2H, $ArCH_2$), 6.66 (d, *J* 8.4 Hz, 1H, ArH), 6.88 (t, *J* 7.3 Hz, 1H, ArH), 7.07 (d, 9.2 Hz, 1H, ArH), 7.15 - 7.21 (m, 2H, ArH), 7.37 (dd, *J* 2.6, 9.2 Hz, 1H, ArH), 7.68 (d, *J* 8.1 Hz, 2H, ArH), 7.83 - 7.87 (m, 2H, ArH), 7.95 (d, *J* 8.78 Hz, 1H, ArH), 8.22 (d, *J* 8.42 Hz, 2H, ArH), 8.40 (app d, *J* 2.2 Hz, 1H, ArH) ppm. ^{13}C NMR (100 MHz, C_6D_6) δ: 13.6, 20.7, 22.2, 25.2, 29.4, 30.2, 37.0, 40.8, 51.8, 99.1, 107.5, 113.9, 116.6, 120.1, 120.3, 121.6, 123.7, 129.5, 129.6, 129.6, 129.7, 130.3, 130.3, 130.8, 132.7, 136.2, 141.5, 145.1, 148.0, 150.8, 150.9, 164.8, 223.3 ppm.

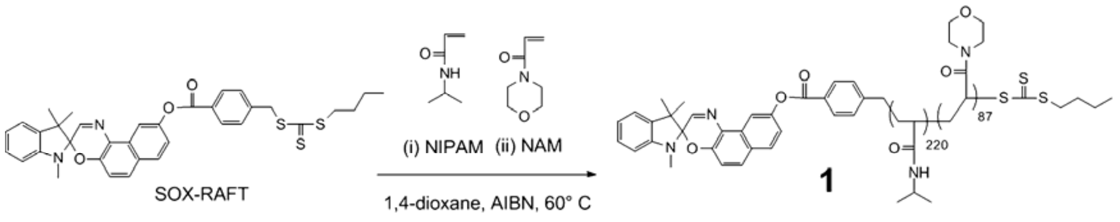


9'-Acrylyloxy-1,3,3-trimethylspiro[indoline-2,3'-[3*H*]naphtho[2,1-*b*][1,4]oxazine], (SOX-ACR). The title compound was synthesized as SOX-RAFT agent above, however using 9'-hydroxy-1,3,3-trimethylspiro[indoline-2,3'-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (1.51 g, 4.38 mmol), acryloyl chloride (0.44 g, 4.83 mmol) and triethylamine (0.67 g, 6.57 mmol) in dry CH_2Cl_2 (40 mL). The reaction mixture was stirred for 2 hours in total and the product obtained as a pale cream solid (1.60 g, 92%) after purification by column chromatography (silica gel, CH_2Cl_2). ^{1}H NMR (400 MHz, d_6-acetone) δ: 1.34 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 2.78 (s, 3H, N-CH_3), 6.14 (dd, *J* 10.55 Hz, *J* 1.46 Hz, 1H, =CH), 6.46 (dd, *J* 17.20 Hz, *J* 10.25 Hz, 1H, =CH), 6.60 -6.67 (m, 2H, =CH and ArH), 6.85 - 6.89 (m, 1H, ArH), 7.05 (d, *J* 8.78 Hz, 1H, ArH), 7.14 - 7.21 (m, 2H, ArH), 7.25 (dd, *J* 2.6, *J* 8.78 Hz, 1H, ArH), 7.82 - 7.84 (m, 2H, ArH), 7.90 (d, *J* 8.78 Hz, 1H, ArH), 8.29 (d, *J* 2.60 Hz, 1H, ArH) ppm. ^{13}C NMR

(100 MHz, d_6-acetone) δ: 21.9; 26.7; 30.7; 53.5; 100.7; 109.0; 114.5; 118.3; 123.2; 121.6; 121.3; 124.8; 129.2; 129.9; 129.7; 131.9; 131.3; 134.1; 133.6; 137.7; 146.6; 149.5; 151.7; 153.1; 166.0 ppm.

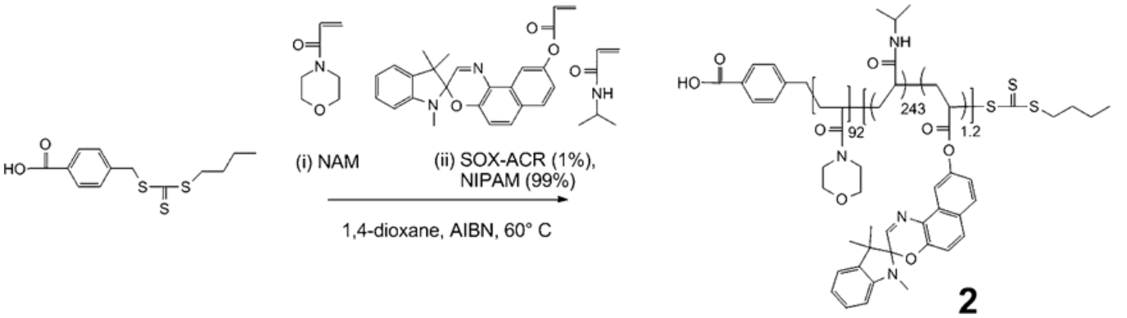
9'-Propionyloxy-1,3,3-trimethylspiro[indoline-2,3'-[3*H*]naphtho[2,1-*b*][1,4]oxazine], (SOX-PROP). The title compound was synthesized using the same procedure as SOX-ACR, however using 9'-hydroxy-1,3,3-trimethylspiro[indoline-2,3'-[3*H*]naphtho[2,1-*b*][1,4]oxazine] (0.20 g, 0.58 mmol), propionyl chloride (0.054 g, 0.58 mmol) and triethylamine (0.106 g, 1.74 mmol) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred for 30 minutes in total and the product obtained as a pale cream solid (0.20 g, 86%) after purification by column chromatography (silica gel, diethyl ether/hexane, 1:1). ^{1}H NMR (400 MHz, d_6-acetone) δ: 1.26 (t, *J* 7.56 Hz, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 2.70 (q, *J* 7.55 Hz, 2H, CH_2), 2.76 (s, 3H, N-CH_3), 6.65 (d, *J* 7.72 Hz, 1H, ArH), 6.83 - 6.91 (m, 1H, ArH), 7.03 (d, *J* 8.87 Hz, 1H, ArH), 7.13 - 7.23 (m, 3H, ArH), 7.77 - 7.89 (m, 3H, ArH), 8.26 (d, *J* 2.37 Hz, 1H, ArH) ppm. ^{13}C NMR (100 MHz, d_6-acetone) δ: 9.1, 20.7, 25.5, 27.8, 29.5, 52.3, 99.5, 107.8, 113.4, 116.7, 120.3, 120.4, 122.1, 123.5, 127.9, 128.6, 129.9, 130.7, 132.4, 136.5, 145.4, 148.3, 150.8, 151.8, 173.1 ppm.

(2) Synthesis of block copolymers, PNIPAM-*block*-PNAM and PBA-*block*-PNAM.



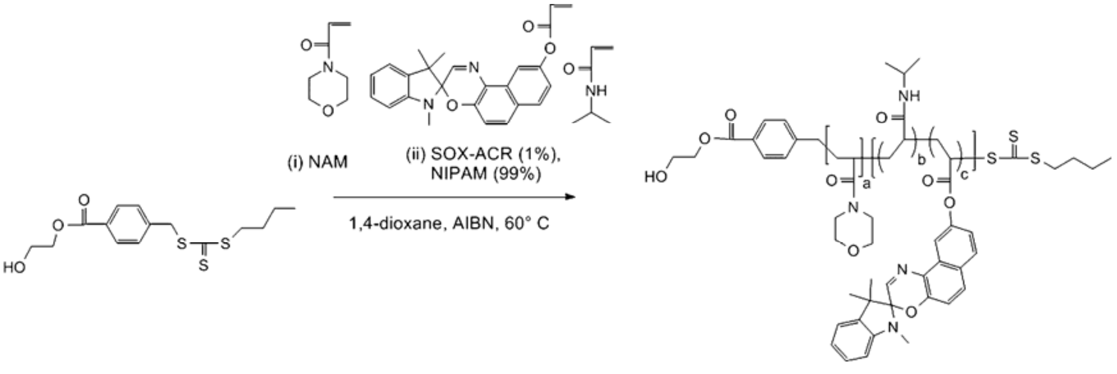
SOX-(NIPAM)$_{220}$-*b*-(NAM)$_{87}$ block copolymer 1. A solution of *N*-isopropyl acrylamide (NIPAM) (4.92g, 43.5 mmol), AIBN (azobisisobutyronitrile) (1.43mg, 8.71 × 10^{-6} mol) and SOX-RAFT agent (109 mg, 0.174 mmol) was prepared in 1,4-dioxane (25 mL). The final ratio of monomer to RAFT agent was 250:1 with 0.02 mol% of AIBN with respect to monomer. The mixture was divided between several ampoules which were then degassed with three freeze-pump-thaw cycles, sealed and then heated at 60 °C in a thermostatted oil bath for up to 16 hours. Conversions were evaluated by ^{1}H nmr by comparing the integration of the vinyl proton from the monomer at 6.6 ppm to the polymeric and monomer signals at 4 ppm from $(CH_3)_2CH$. The final polymers were purified precipitation into diethyl ether 2 × and vacuum drying till constant weight. Polymerization result for PNIPAM macro RAFT agent: time 16 hours; conversion = 88%; M_n 35,050 g/mol, PDI 1.10 (GPC-DMF); M_n 25,490 g/mol (^{1}H NMR estimate); M_n 25,520 g/mol (theoretical M_n).

The macro RAFT agent was used for subsequent block extension with *N*-acryloyl morpholine (NAM): A solution of NAM (0.41 g, 2.88 mmol), the PNIPAM macro RAFT agent (0.80 g, 3.14×10^{-5} mol), AIBN (0.25 mg, 1.52×10^{-6} mol) was prepared and transferred to an ampoule using 1,4-dioxane (*ca.* 2.5 mL). The final ratio of monomer to RAFT agent was 92:1 with 0.05 mol% of AIBN with respect to monomer. The ampoule was then degassed with three freeze-pump-thaw cycles, sealed and then heated at 60 °C in a thermostatted oil bath for 16 hours. The final conversion was evaluated gravimetrically on a small sample after removal of monomer and solvent and drying, in a vacuum oven until constant weight. Polymerization result for SOX-$(NIPAM)_{220}$-*b*-$(NAM)_{87}$ **1**: time 16 hours; conversion = 90%; M_n 47,470 g/mol, PDI 1.16 (GPC-DMF); M_n 38,360 g/mol (^{1}H NMR estimate); M_n 37,800 g/mol (theoretical M_n). GPC plots showing sequential block formation of the copolymer are displayed in section (4).



$[(NIPAM)_{243}$-*co*-$(SOX)_{1.2}]$-*b*-$[NAM]_{92}$ block copolymer 2. A solution of NAM (2.45g, 17.4 mmol), AIBN (2.70 mg, 1.74×10^{-5} mol) and RAFT agent **5** (55 mg, 0.183 mmol) was completely transferred to an ampoule using 1,4-dioxane (*ca.* 10 mL). The final ratio of monomer to RAFT agent was 95:1 with 0.1 mol% of AIBN with respect to monomer. The ampoule was then degassed with three freeze-pump-thaw cycles, sealed and then heated at 60 °C in a thermostatted oil bath for 4 hours and 30 minutes. The final conversion was evaluated gravimetrically on a small sample after removal of monomer and solvent and drying, in a vacuum oven until constant weight. For GPC evaluation, a small sample of the polymer was modified by methylation of the carboxylic acid end-group with trimethylsilyldiazomethane, using a procedure reported in literature (Couvreur L. *et al*, Macromolecules, 2003, 36 (22), p8261). Polymerization result for PNAM macro RAFT agent: conversion = 95%; M_n 15,600 g/mol, PDI 1.03 (GPC-DMF); M_n 13,300 g/mol (^{1}H NMR estimate); M_n 13,040 g/mol (theoretical M_n).

The PNAM macro RAFT agent was used for subsequent block extension with NIPAM and SOX-ACR: A solution of NIPAM (1.45 g, 12.77 mmol), SOX-AC (51.4 mg, 0.129 mmol), the PNAM macro RAFT agent (0.687 g, 5.17×10^{-5} mol) and AIBN (2.12 mg, 1.29×10^{-5} mol) was prepared and transferred to an ampoule using 1,4-dioxane (*ca.* 5 mL). The final ratio of monomers to RAFT agent was 250:1 with 0.1 mol% of AIBN with respect to monomers. The ampoule was then degassed with three freeze-pump-thaw cycles, sealed and then heated at 60 °C in a thermostatted oil bath for 16 hours. The conversions of NIPAM to polymer was evaluated by ^{1}H nmr by comparing the integration of the vinyl proton from the monomer at 6.6 ppm to the polymeric and monomer signals at 4 ppm from $(CH_3)_2CH$. The SOX-ACR appeared to be fully consumed. The final polymers were purified precipitation into diethyl ether 2 × and vacuum drying till constant weight. For GPC evaluation, a small sample of the polymer was modified by methylation as described above. Polymerization result for $[(NIPAM)_{243}$-*co*-$(SOX)_{1.2}]$-*b*-$[NAM]_{92}$ **2**: conversion = 95%; M_n 57,790 g/mol, PDI 1.16 (GPC-DMF); M_n 41,300 g/mol (^{1}H NMR estimate); M_n 40,180 g/mol (theoretical M_n). GPC plots showing sequential block formation of the copolymer are displayed section (4).

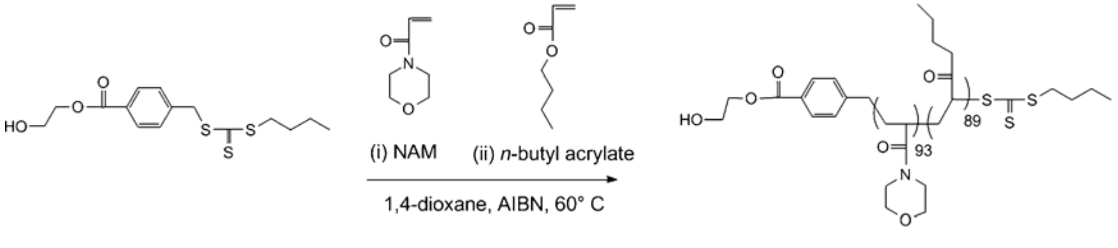


[(NIPAM)$_{115}$-*co*-(SOX)$_{1.3}$]-*b*-[NAM]$_{93}$, 3 and [(NIPAM)$_{178}$-*co*-(SOX)$_{1.6}$]-*b*-[NAM]$_{93}$, 4 block copolymers. A solution of NAM (6.20 g, 43.9 mmol), AIBN (7.14 mg, 4.35 × 10^{-5} mol) and 2-hydroxyethyl-4-(*n*-butylsulfanylthiocarbonyl)sulfanyl methyl benzoate (158 mg, 0.458 mmol) was completely transferred to an ampoule using 1,4-dioxane (*ca.* 25 mL). The final ratio of monomer to RAFT agent was 96:1 with 0.1 mol% of AIBN with respect to monomer. The ampoule was then degassed with three freeze-pump-thaw cycles, sealed and then heated at 60 °C in a thermostatted oil bath for 3 hours. The final conversion was evaluated gravimetrically on a small sample after removal of monomer and solvent and drying in a vacuum oven until constant weight. Polymerization result for PNAM macro RAFT agent: conversion = 97%; M_n 13,300 g/mol, PDI 1.05 (GPC-DMF); M_n 13,600 g/mol (^{1}H NMR estimate); M_n 13,150 g/mol (theoretical M_n).

The macro RAFT agent was used for subsequent block extension with NIPAM and SOX-ACR: A solution of NIPAM (2.06 g, 14.59 mmol), SOX-ACR (74.0 mg, 0.129 mmol), the aforementioned PNAM macro RAFT agent (1.05 g, 7.72 × 10^{-5} mol) and AIBN (3.0 mg, 1.83 × 10^{-5} mol) was prepared using 1,4-dioxane (*ca.* 8.5 mL) and split into two ampoules. The final ratio of monomers to RAFT agent in each was 250:1 with 0.1 mol% of AIBN with respect to monomers. The ampoules were then degassed with three freeze-pump-thaw cycles, sealed and then heated at 60 °C in a thermostatted oil bath for 50 minutes and 2 hours. The conversions of NIPAM to polymer was evaluated by ^{1}H nmr by comparing the integration of the vinyl proton from the monomer at 6.6 ppm to the polymeric and monomer signals at 4 ppm from $(CH_3)_2CH$. The SOX-ACR appeared to be fully consumed. The final polymers were purified precipitation into diethyl ether 2 × and vacuum drying until constant weight was achieved.

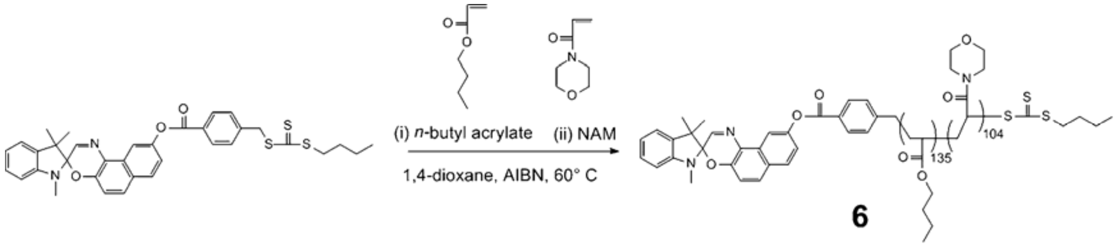
Polymerization result for $[(\text{NIPAM})_{115}$-*co*-$(\text{SOX})_{1.3}]$-*b*-$[\text{NAM}]_{93}$, **3**: time = 50 minutes, conversion = 55%; M_n 27,200 g/mol, PDI 1.16 (GPC-DMF); M_n 26,800 g/mol (^{1}H NMR estimate); M_n 29,160 g/mol (theoretical M_n).

Polymerization result for $[(\text{NIPAM})_{178}$-*co*-$(\text{SOX})_{1.6}]$-*b*-$[\text{NAM}]_{93}$, **4**: time = 2 hours, conversion = 72%; M_n 35,350 g/mol, PDI 1.22 (GPC-DMF); M_n 34,080 g/mol (^{1}H NMR estimate); M_n 33,970 g/mol (theoretical M_n). GPC plots showing sequential block formation of the copolymers are displayed in section (4).



5

(n-BA)$_{89}$-*b*-(NAM)$_{93}$ block copolymer 5. Block copolymer **5** was synthesised by the extension of the same PNAM macro RAFT agent as used above. A solution of *n*-butyl acrylate (*n*-BA) (1.41 g, 11.0 mmol), the aforementioned PNAM macro RAFT agent (1.0 g, 7.35×10^{-5} mol) and AIBN (1.5 mg, 9.10×10^{-6} mol) was transferred into an ampoule using 1,4-dioxane (*ca.* 2 mL). It was then degassed with three freeze-pump-thaw cycles, sealed and heated at 60 °C in a thermostatted oil bath for 6 hours. The final ratio of monomers to RAFT agent was 150:1 with 0.08 mol% of AIBN with respect to monomer. The conversion was evaluated by ^{1}H nmr. The resonances integrated to obtain conversions were the vinyl peaks at 5.8, 6.2 and 6.4 ppm (monomer only) and the OCH_2-peaks at 3.9 - 4.1 ppm (monomer and polymer). The polymer was then purified by evaporation of excess monomer over a gentle stream of N_2, dissolution of the crude mixtures into CH_2Cl_2, precipitation into methanol and decanting the supernatant liquid. Precipitation was carried out 2 × and the polymer was then dried in a vacuum oven for 48 hours. Polymerization result for (n-BA)$_{89}$-*b*-(NAM)$_{93}$ **5**: conversion = 64%; M_n 21,328 g/mol, PDI 1.20 (GPC-DMF); M_n 24,881 g/mol (^{1}H NMR estimate); M_n 25,900 g/mol (theoretical M_n). GPC plots showing sequential block formation of the copolymer are displayed in section (4).

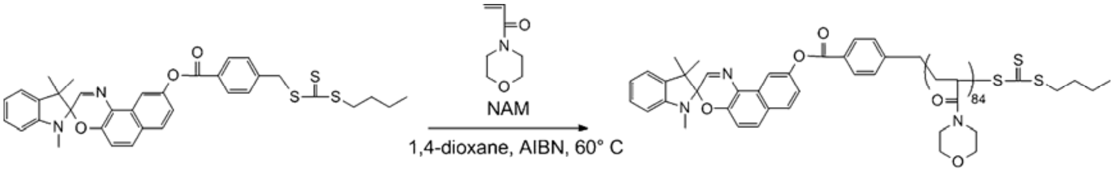


6

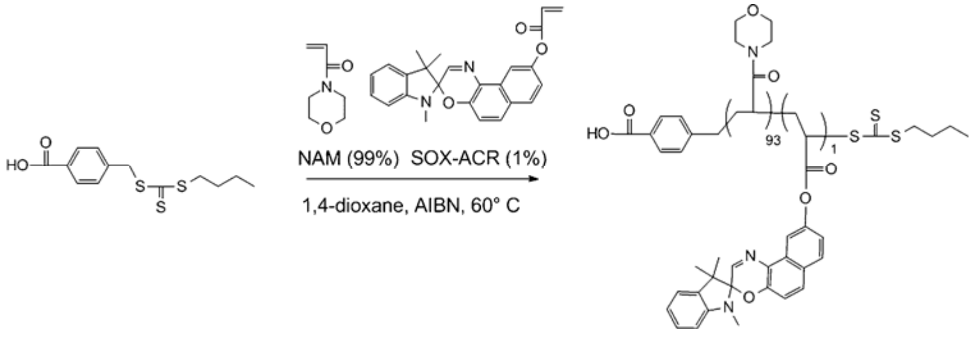
SOX-(*n*-BA)$_{135}$-*b*-(NAM)$_{104}$ block copolymer 6. A solution of *n*-BA (7.05 g, 55.0 mmol), AIBN (3mg, 1.84 ×10^{-5} mol) and SOX-RAFT agent (230 mg, 0.367 mmol) was prepared in benzene (10 mL). The final ratio of monomer to RAFT agent was 150:1 with 0.03 mol% of AIBN with respect to monomer. The mixture was transferred to an ampoule which was then degassed with three freeze-pump-thaw cycles, sealed and then heated at 60 °C in a thermostatted oil bath for 8 hours. The conversion was evaluated by ^{1}H nmr. The resonances integrated were the vinyl peaks at 5.8, 6.2 and 6.4 ppm (monomer only) and the OCH$_2$- peaks at 3.9 - 4.1 ppm (monomer and polymer). The polymer was then purified by evaporation of excess monomer over a gentle stream of N$_2$, dissolution of the crude mixtures into CH$_2$Cl$_2$, precipitation into methanol and decanting the supernatant liquid. Precipitation was carried out 2 × and the polymer then dried in a vacuum oven for 48 hours. Polymerization result for poly(*n*-butyl acrylate), PBA macro RAFT agent: conversion = 84%; M_n 20,430 g/mol, PDI 1.04 (GPC-DMF); M_n 17,980 g/mol (^{1}H NMR estimate); M_n 16,790 g/mol (theoretical M_n).

The PBA macro RAFT agent was used for subsequent block extension with NAM: A solution of NAM (1.20g, 8.50 mmol), the aforementioned PBA macro RAFT agent (1.30g, 7.23 × 10^{-5} mol) and AIBN (0.64 mg, 3.90 × 10^{-6} mol) was prepared and transferred to an ampoule using 1,4-dioxane (*ca.* 6 mL). The final ratio of monomer to RAFT agent was 118:1 with 0.05 mol% of AIBN with respect to monomer. The ampoule was then degassed with three freeze-pump-thaw cycles, sealed and then heated at 60 °C in a thermostatted oil bath for 16 hours. The polymer was then purified by dissolution of the crude mixtures into CH$_2$Cl$_2$, precipitation into methanol and decanting the supernatant liquid. Precipitation was carried out 2 × and the polymer was then dried in a vacuum oven for 48 hours. The final conversion was evaluated gravimetrically on a small sample after removal of monomer and solvent and drying, in a vacuum oven until constant weight. Polymerization result for SOX-(*n*-BA)$_{135}$-*b*-(NAM)$_{104}$ block copolymer **6**: conversion = 85%; M_n 35,680 g/mol, PDI 1.06 (GPC-DMF); M_n 32,690 g/mol (^{1}H NMR estimate); M_n 32,140 g/mol (theoretical M_n). GPC plots showing sequential block formation of the copolymer are displayed in section (4).

(3) Synthesis of PNAM control polymers:

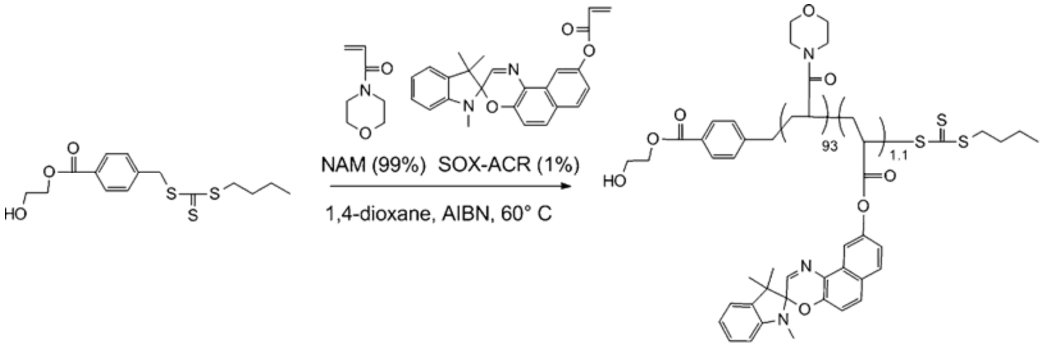


Control polymer SOX-(NAM)$_{84}$. A solution of NAM (1.46 g, 10.3 mmol), AIBN (1.4 mg, 8.84 × 10^{-6} mol) and SOX-RAFT agent (68 mg, 0.109 mmol) was transferred to an ampoule using 1,4-dioxane (*ca.* 5 mL). The final ratio of monomer to RAFT agent was 95:1 with 0.09 mol% of AIBN with respect to monomer. The ampoule was then degassed with three freeze-pump-thaw cycles, sealed and then heated at 60 °C in a thermostatted oil bath for 16 hours. The final conversion was evaluated gravimetrically on a small sample after removal of monomer and solvent and drying, in a vacuum oven until constant weight. Polymerization result for SOX-(NAM)$_{84}$: conversion = 90%; M_n 14,300 g/mol, PDI 1.04 (GPC-DMF); M_n 12,450 (^{1}H NMR estimate); M_n 11,360 g/mol (theoretical M_n).



Control polymer (SOX)$_1$-*co*-(NAM)$_{93}$. A solution of NAM (2.43g, 17.2 mmol), SOX-ACR (69 mg, 0.174 mmol), AIBN (2.90 mg, 1.74 × 10^{-5} mol) and 4-(*n*-butylsulfanylthiocarbonyl)sulfanyl methylbenzoic acid RAFT agent (55 mg, 0.183

mmol) was transferred to an ampoule using 1,4-dioxane (*ca.*10 mL). The final ratio of monomers to RAFT agent was 95:1 with 0.1 mol% of AIBN with respect to monomer. The ampoule was then degassed with three freeze-pump-thaw cycles, sealed and then heated at 60 °C in a thermostatted oil bath for 4 hours and 30 minutes. The final conversion was evaluated gravimetrically on a small sample after removal of monomer and solvent and drying, in a vacuum oven until constant weight. For GPC evaluation, a small sample of the polymer was modified by methylation of the carboxylic acid end-group with trimethylsilyldiazomethane, using a procedure reported in literature (Couvreur L. *et al*, Macromolecules, 2003, 36 (22), p8261). Polymerization result for $(SOX)_1$-*co*-$(NAM)_{93}$ polymer: conversion = 98%; M_n 20,132 g/mol, PDI 1.03 (GPC-DMF); M_n 13,900 g/mol (^{1}H NMR estimate); M_n 13,440 g/mol (theoretical M_n).



Control polymer $(SOX)_{1.1}$-*co*-$(NAM)_{93}$. A solution of NAM (1.22 g, 8.64 mmol), SOX-ACR (34.7 mg, 8.71 × 10^{-5} mmol), AIBN (1.43 mg, 0.871 × 10^{-5} mol) and 2-hydroxyethyl-4-(*n*-butylsulfanylthiocarbonyl)sulfanyl methyl benzoate RAFT agent (32.3 mg, 9.38 × 10^{-5} mol) was transferred to an ampoule using 1,4-dioxane (*ca.* 5 mL). The final ratio of monomer to RAFT agent was 93:1 with 0.1 mol% of AIBN with respect to monomers. The ampoule was then degassed with three freeze-pump-thaw cycles, sealed and then heated at 60 °C in a thermostatted oil bath for 4 hours. The final conversion was evaluated gravimetrically on a small sample after removal of monomer and solvent and drying, in a vacuum oven until constant weight. Polymerization result for $(SOX)_{1.1}$-*co*-$(NAM)_{93}$: conversion = 95%; M_n 12,930 g/mol, PDI 1.05 (GPC-DMF); M_n 13,600 g/mol (^{1}H NMR estimate); M_n 12,700 g/mol (theoretical M_n).

(4) GPC Traces showing block formation for polymers 1-6

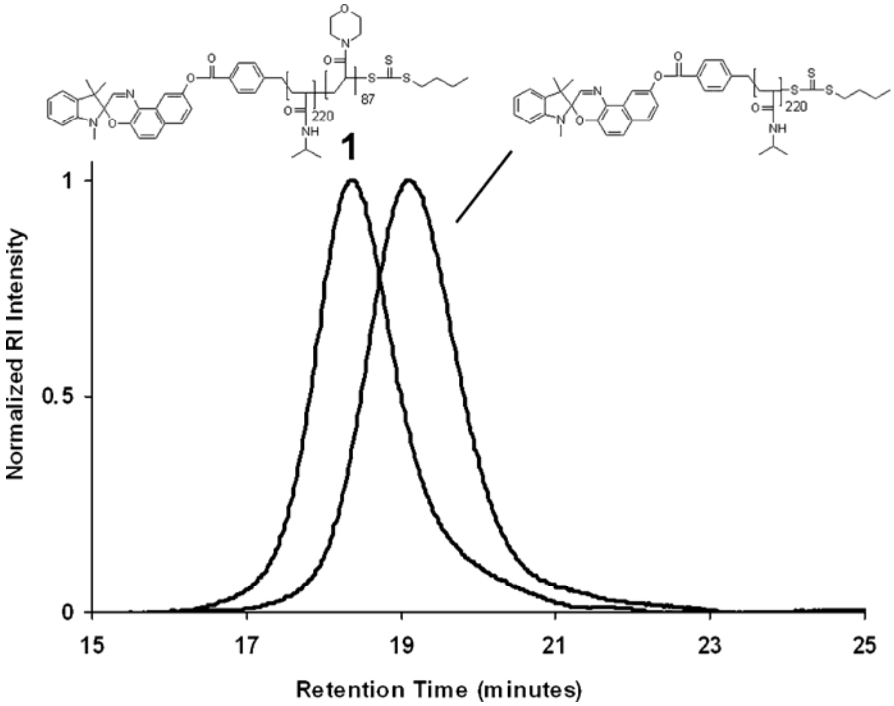


Figure 1. Overlaid and normalised GPC traces showing sequential block formation for synthesis of SOX-(NIPAM$_{)220}$-*b*-(NAM)$_{87}$ **1**.

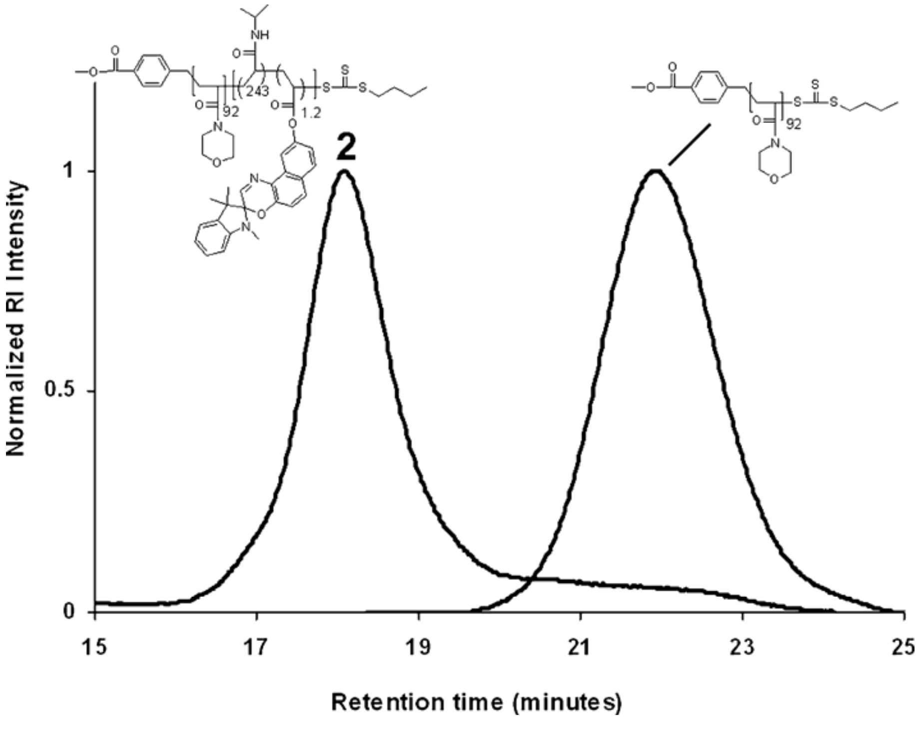


Figure 2. Overlaid and normalised GPC traces showing sequential block formation for synthesis of [(NIPAM)$_{243}$-*co*-(SOX)$_{1.2}$]-*b*-[NAM]$_{92}$ **2**.

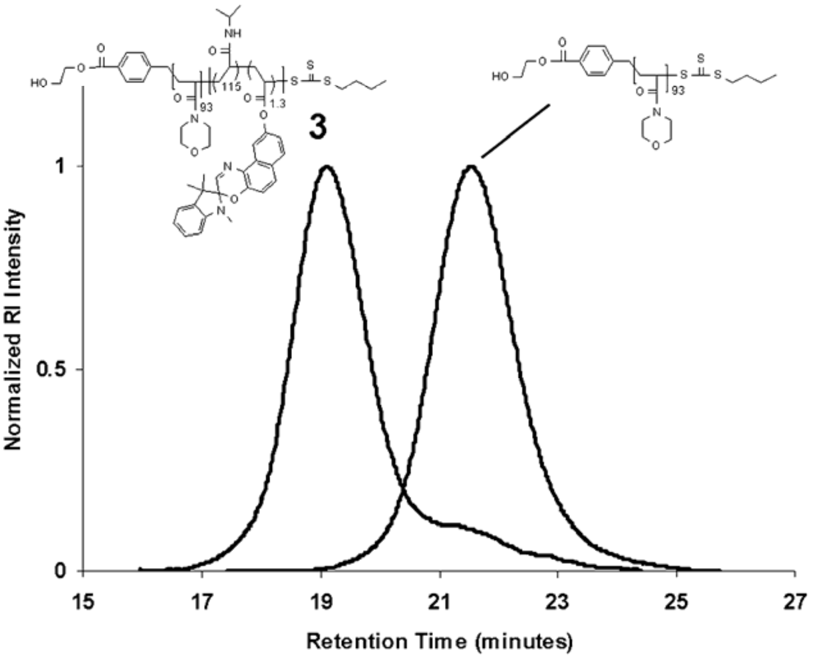


Figure 3. Overlaid and normalised GPC traces showing sequential block formation for synthesis of [$(NIPAM)_{115}$-*co*-$(SOX)_{1.3}$]-*b*-$[NAM]_{93}$ **3**.

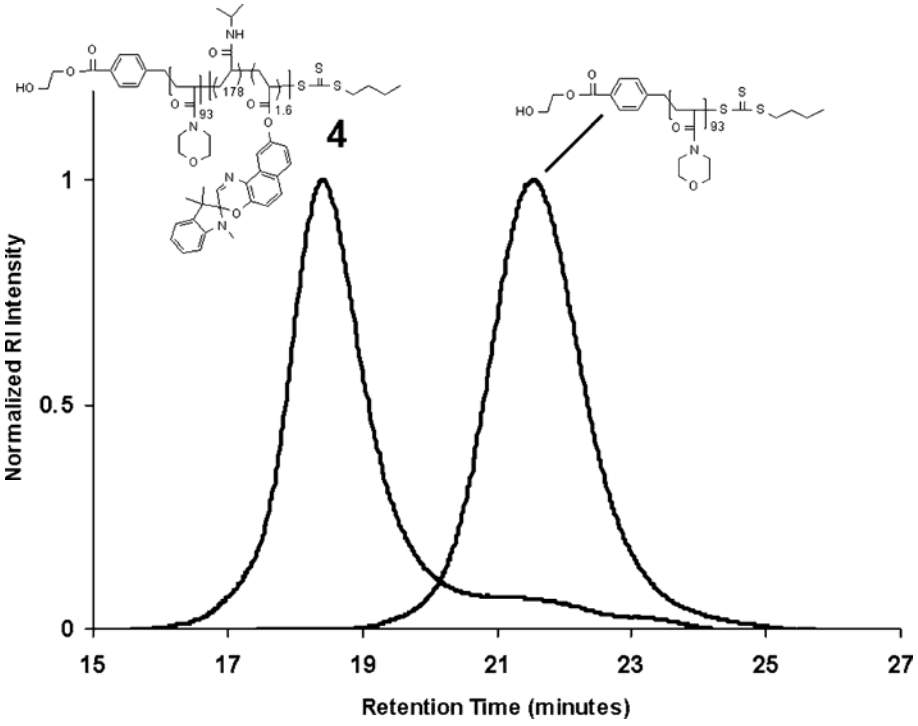


Figure 4. Overlaid and normalised GPC traces showing sequential block formation for synthesis of [$(NIPAM)_{178}$-*co*-$(SOX)_{1.6}$]-*b*-$[NAM]_{93}$ **4**.

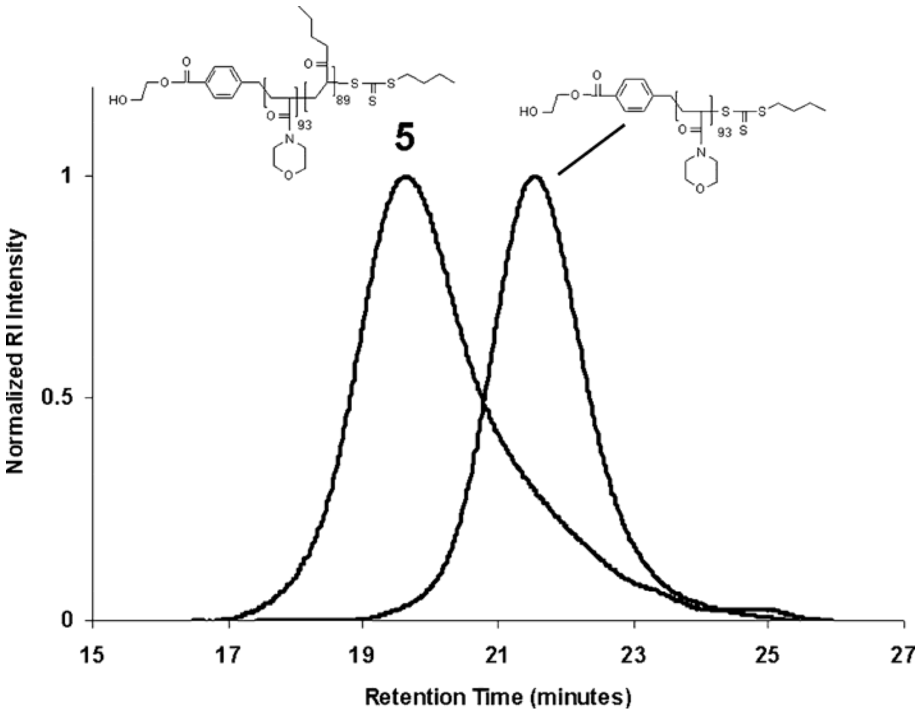


Figure 5. Overlaid and normalised GPC traces showing sequential block formation for synthesis of $(BA)_{89}$-*b*-$(NAM)_{93}$ **5**.

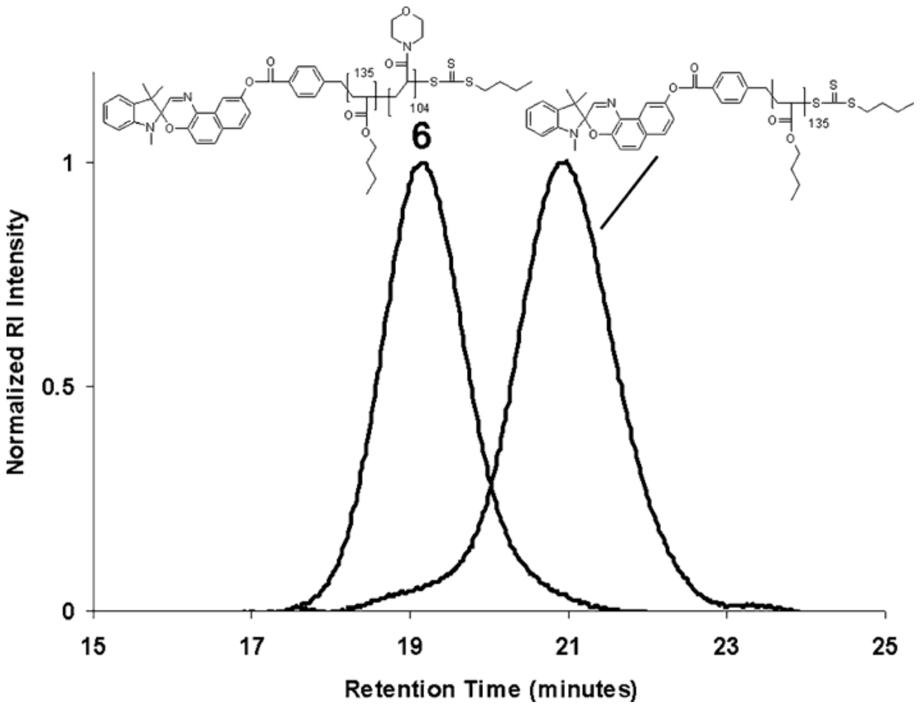


Figure 6. Overlaid and normalised GPC traces showing sequential block formation for synthesis of SOX-$(BA)_{135}$-*b*-$(NAM)_{104}$ **6**.

(5) Representative ^{1}H NMR Spectra of Polymers

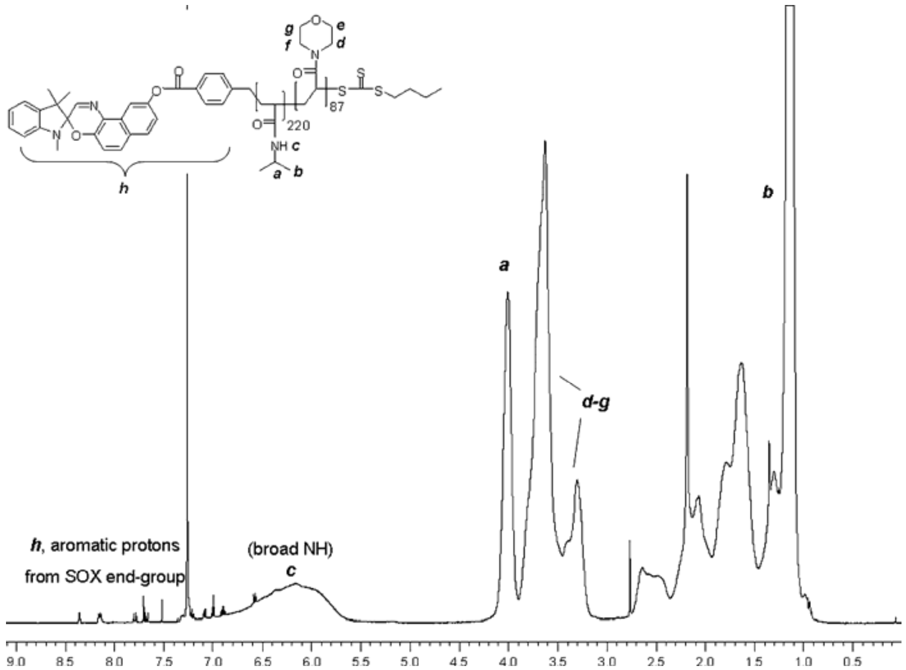


Figure 7. ^{1}H NMR (400 MHz, CDCl$_3$) of of SOX-(NIPAM)$_{220}$-*b*-(NAM)$_{87}$ **1**.

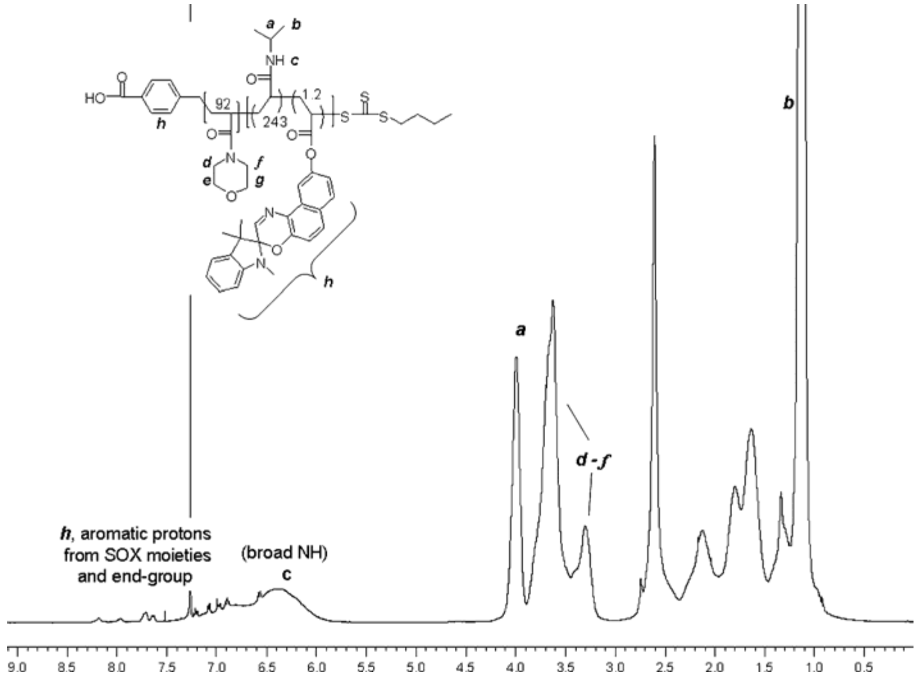


Figure 8. ^{1}H NMR (400 MHz, CDCl$_3$) of [(NIPAM)$_{243}$-*co*-(SOX)$_{1.2}$]-*b*-[NAM]$_{92}$ **2**.

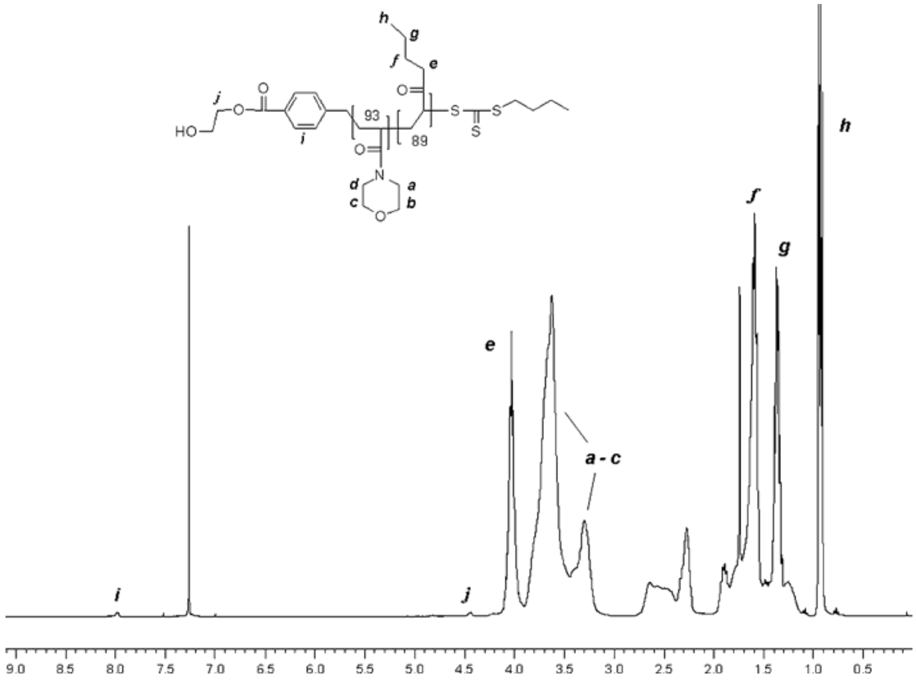


Figure 9. ^{1}H NMR (400 MHz, $CDCl_3$) of $(BA)_{89}$-*b*-$(NAM)_{93}$ **5**.

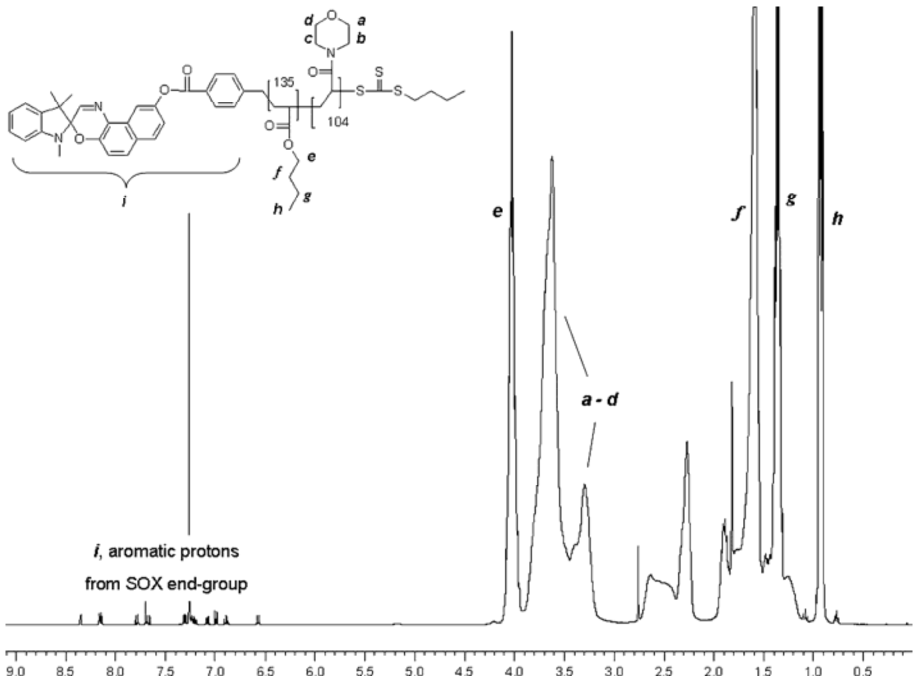


Figure 10. ^{1}H NMR (400 MHz, $CDCl_3$) of SOX-$(BA)_{135}$-*b*-$(NAM)_{104}$ **6**.

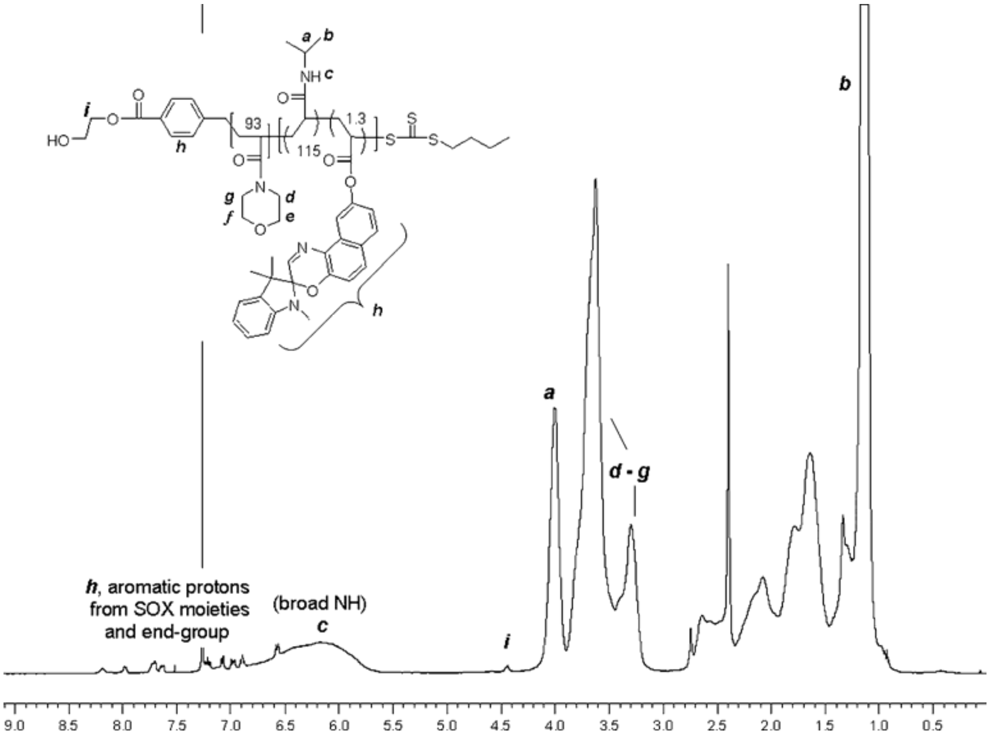


Figure 11. ^{1}H NMR (400 MHz, $CDCl_3$) of $[(NIPAM)_{115}$-*co*-$(SOX)_{1.3}]$-*b*-$[NAM]_{93}$ **3**.

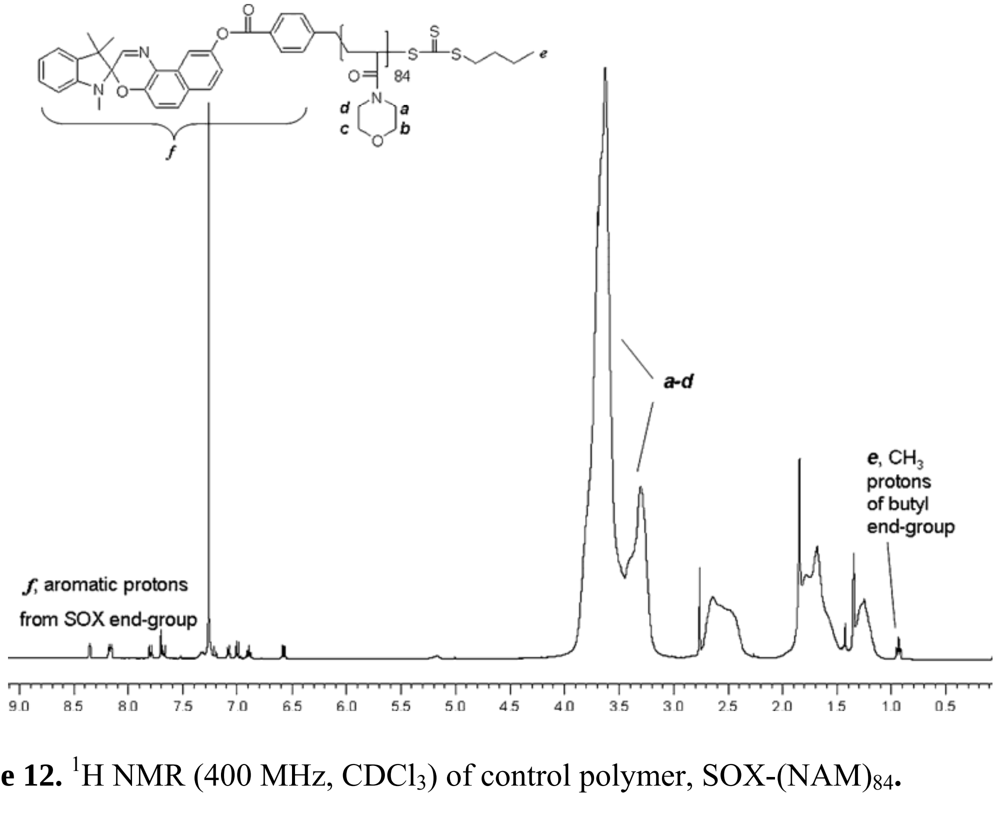


Figure 12. ^{1}H NMR (400 MHz, $CDCl_3$) of control polymer, SOX-$(NAM)_{84}$**.**

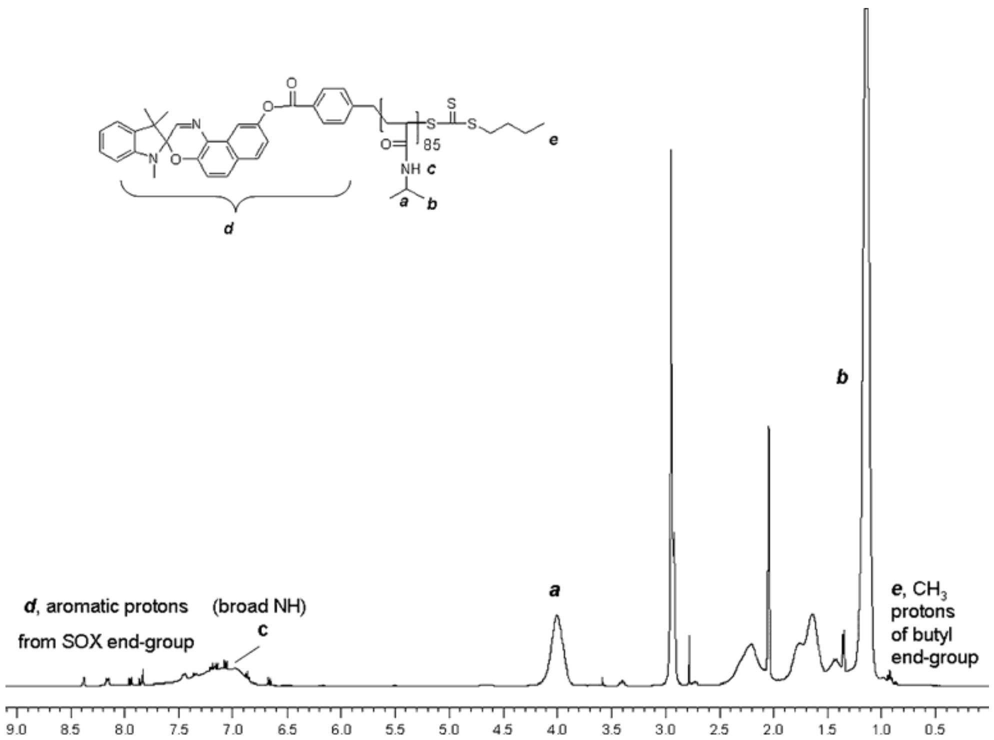


Figure 13. ^{1}H NMR (400 MHz, d_6-acetone) of SOX-PNIPAM (macroRAFT precursor to **1**).

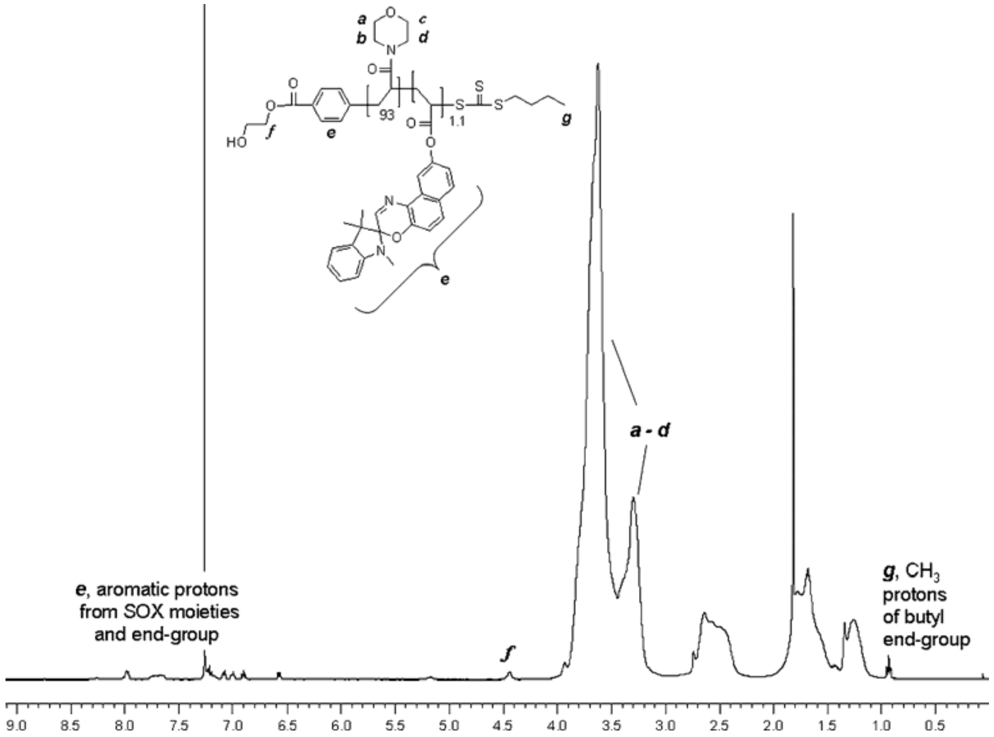


Figure 14. ^{1}H NMR (400 MHz, CDCl$_3$) of control polymer (SOX)$_{1.1}$-*co*-(NAM)$_{93}$.

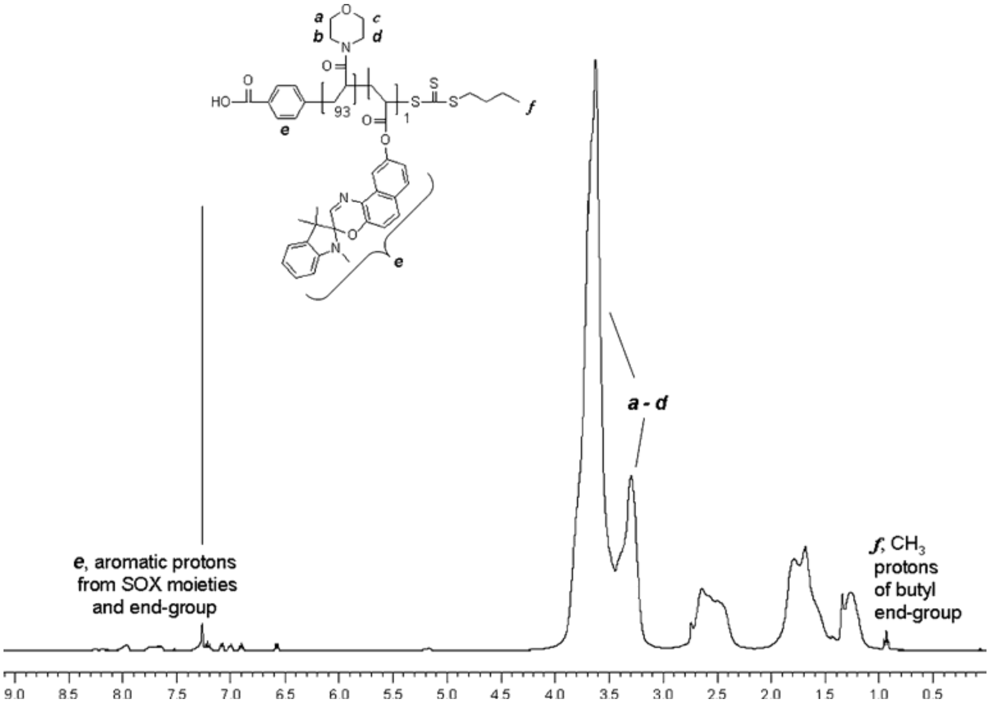


Figure 15. ^{1}H NMR (400 MHz, CDCl$_3$) of control polymer (SOX)1-*co*-(NAM)$_{93}$.

(6) Raw Data for Graphs

Table 1: Decolouration kinetics of SOX-(NIPAM)$_{220}$-*b*-(NAM)$_{87}$ **1** in water (left) and corresponding DLS measurements (right) *vs* temperature (ºC).[a]

Temp. (ºC)	A_0[b]	k_1 (min^{-1})	A_1	k_2 (min^{-1})	A_2
20	1.68	1.2827	1.0276	0	0
22	1.32	1.6914	1.0348	0	0
24	1.18	2.0510	1.0316	0	0
26	1.00	2.4756	1.0223	0	0
28	0.94	3.1881	1.0168	0	0
29	0.85	3.5694	1.0031	0.0955	0.0061
30	0.75	3.9134	1.0068	0.2343	0.0070
31	0.59	4.1654	1.0031	0.2459	0.0114
32	0.51	4.5874	0.9888	0.7949	0.0173
33	0.53	5.0984	0.9906	0.7390	0.0194
34	0.43	4.9654	0.9773	0.3966	0.0288
36	0.42	6.3568	1.0129	0	0
38	0.33	8.4718	0.9969	1.0428	0.0121

Temp. (ºC)	D_h (nm) PDI
20	29.5 0.053
22	29.5 0.066
24	29.5 0.067
26	29.5 0.063
28	30.0 0.057
30	30.8 0.078
32	34.4 0.058
34	47.7 0.029
35	49.4 0.014
38	49.4 0.004

[a] Refer to above experimental section for description of measurements; for both measurements concentration of polymer in water = 1.2×10^{-4} M (4.8 mg/mL), based on M_n 38,360 g/mol (^{1}H NMR estimate).

[b] A_0 refers to measured absorbance intensity at onset of thermal decolouration period

Table 2: Decolouration of [(NIPAM)$_{243}$-*co*-(SOX)$_{1.2}$]-*b*-[NAM]$_{92}$ **2** in water (left) and corresponding DLS measurements (right) *vs* temperature (ºC).[a]

Temp. (º C)	A_0[b]	k_1 (min^{-1})	A_1	k_2 (min^{-1})	A_2
20	1.37	2.8930	0.9648	0.9634	0.0435
22	1.20	3.6255	0.9809	1.0076	0.0219
24	1.18	4.6339	0.9615	1.3115	0.0455
26	0.96	5.9048	0.9416	1.7016	0.0602
27	0.91	6.4137	0.9663	1.4622	0.0434
28	0.85	6.8381	1.0212	0.4800	0.0077
29	0.83	6.6726	1.0175	0.3345	0.0066
30	0.81	6.6116	1.0080	0.2912	0.0052
31	0.77	6.7862	1.0121	0.0212	0.0012
32	0.70	7.2285	0.9936	0.7604	0.0069
34	0.59	9.8620	0.9542	4.0762	0.0507
36	0.55	10.736	1.0222	0	0
38	0.45	13.662	1.0249	0	0

Temp. (ºC)	D_h (nm) PDI
20	15.6 0.266
22	15.8 0.282
25	15.9 0.275
27	17.9 0.236
28	21.7 0.232
29	25.5 0.208
30	28.3 0.159
32	30.3 0.146
35	30.1 0.140

[a] Refer to above experimental section for description of measurements; for both measurements concentration of polymer in water = 1.0 × 10^{-4} M (4.1 mg/mL), based on M_n 41,300 g/mol (^{1}H NMR estimate); refer to figures below for plotted results

[b] A_0 refers to measured absorbance intensity at onset of thermal decolouration period

Table 3: Decolouration of [(NIPAM)$_{115}$-*co*-(SOX)$_{1.6}$]-*b*-[NAM]$_{93}$ **3** in water and corresponding DLS measurements (right) *vs* temperature (ºC).[a]

Temp. (º C)	A_0[b]	k_1 (min^{-1})	A_1	k_2 (min^{-1})	A_2
20	1.80	3.4757	0.9596	0.6265	0.0454
22	1.57	4.4044	0.9554	0.7937	0.0460
24	1.36	5.4194	0.9641	0.8513	0.0387
26	1.16	6.7162	0.9734	1.1720	0.0394
27	1.09	7.2531	0.9665	0.9499	0.0376
28	1.02	7.8480	0.9703	1.0941	0.0401
29	0.95	8.1726	0.9742	0.7973	0.0289
30	0.92	8.5503	0.9641	1.1322	0.0346
31	0.86	8.9601	0.9863	1.3305	0.0362
32	0.82	9.5209	0.9858	1.6122	0.0141
33	0.78	9.9528	0.9975	1.2508	0.0313
34	0.73	11.1090	0.9841	2.0449	0.0535
36	0.64	13.4440	0.9589	3.0696	0.0555
38	0.54	16.7220	0.9361	4.4444	0.0736

Temp. (ºC)	D_h (nm) PDI
20	18.1 0.252
22	18.2 0.233
24	19.1 0.226
26	20.9 0.196
27	22.6 0.167
28	25.2 0.127
30	30.1 0.058
32	33.6 0.017
33	33.9 0.006
34	34.2 0.010
36	34.4 0.006

[a] Refer to above experimental section for description of measurements; for both measurements concentration of polymer in water = 1.3 × 10^{-4} M (3.5 mg/mL), based on M_n 26,830 g/mol (^{1}H NMR estimate); refer to figures below for plotted results

[b] A_0 refers to measured absorbance intensity at onset of thermal decolouration period.

Table 4: Decolouration of $[(\mathrm{NIPAM})_{178}\text{-}co\text{-}(\mathrm{SOX})_{1.6}]\text{-}b\text{-}[\mathrm{NAM}]_{93}$ **4** in water and corresponding DLS measurements (right) *vs* temperature (ºC).[a]

Temp. (º C)	A_0[b]	k_1 (min^{-1})	A_1	k_2 (min^{-1})	A_2
20	1.87	3.7376	0.9746	0.6778	0.0390
22	1.62	4.5608	0.9873	0.9322	0.0309
24	1.41	5.6587	1.0177	0.9602	0.0205
26	1.24	6.7994	0.9929	0.71055	0.0171
28	1.13	7.7877	1.0126	0.9268	0.0236
30	1.02	8.3080	0.9763	1.1316	0.0288
31	0.97	8.6960	0.9692	1.2508	0.0331
32	0.90	9.2352	0.9607	1.4925	0.0382
33	0.85	9.7262	0.9533	2.2974	0.0450
34	0.79	10.401	0.9717	1.6842	0.0263
36	0.72	12.536	0.9681	2.2300	0.0291
38	0.61	15.114	0.9738	4.6185	0.0281

Temp. (ºC)	D_h (nm) PDI
20	16.9 0.244
22	17.3 0.235
24	18.2 0.227
26	20.6 0.199
27	24.1 0.175
28	29.0 0.130
30	38.1 0.035
32	39.3 0.007
33	39.5 0.017
36	40.0 0.016

[a] Refer to above experimental section for description of measurements; for both measurements concentration of polymer in water = 1.2×10^{-4} M (4.2 mg/ml), based on M_n 34,080 g/mol (^{1}H NMR estimate); refer to figures below for plotted results.

[b] A_0 refers to measured absorbance intensity at onset of thermal decolouration period.

Table 5: Decolouration kinetics of SOX-(NAM)$_{84}$ in water *vs* temperature (ºC).[a]

Temp. (º C)	A_0[b]	k_1 (min^{-1})	A_1	k_2 (min^{-1})	A_2
20	1.83	1.4731	1.0144	1.4747	0.0192
22	1.68	2.0700	1.0092	2.0775	0.0305
24	1.42	2.5766	1.0066	2.5826	0.0314
26	1.10	3.3058	1.0068	3.3077	0.0194
28	0.98	4.1507	1.0065	4.1515	0.0160
30	0.85	5.2334	1.0066	5.2422	0.0167
32	0.69	6.5120	1.0084	6.5153	0.0159
34	0.58	8.1762	1.0097	8.1807	0.0254
36	0.45	10.454	1.0469	10.4900	0.0066

[a] Refer to above experimental section for description of measurements; for both measurements concentration of polymer in water = 1.2 × 10^{-4} M (1.6 mg/ml) based on M_n 12,450 g/mol (^{1}H NMR estimate); refer to figure below for plotted result.

[b] A_0 refers to measured absorbance intensity at onset of thermal decolouration period.

Table 6: Decolouration kinetics of (NAM)$_{93}$-*co*-(SOX)$_1$ in water *vs* temperature (ºC).[a]

Temp. (º C)	A_0[b]	k_1 (min^{-1})	A_1	k_2 (min^{-1})	A_2
20	0.87	2.1497	0.9074	0.6814	0.1140
22	0.53	2.7806	0.8926	0.9224	0.1264
24	0.34	3.2975	0.7834	1.2658	0.2164
26	0.21	3.8182	0.8807	1.0603	0.1124
28	0.14	4.7410	0.8920	1.1823	0.1060
30	0.10	6.0363	0.8788	1.4281	0.1249
32	0.07	7.0123	0.9076	0.5703	0.0832
34	0.05	8.3058	0.9311	0.4430	0.0450
36	0.04	9.5338	0.8900	0.0298	0.0645

[a] Refer to above experimental section for description of measurements; for both measurements concentration of polymer in water = 1.2 × 10^{-4} M (1.7 mg/mL) based on M_n 13,900 g/mol (^{1}H NMR estimate); refer to figure below for plotted result.

[b] A_0 refers to measured absorbance intensity at onset of thermal decolouration period.

Table 7: Decolouration kinetics of $(NAM)_{93}$-*co*-$(SOX)_{1.1}$ in water *vs* temperature (ºC).[a]

Temp. (º C)	A_0[b]	k_1 (min^{-1})	A_1	k_2 (min^{-1})	A_2
20	1.46	2.8557	0.8196	0.8771	0.2148
22	1.32	3.3313	0.8700	0.9638	0.1526
24	1.16	3.8843	0.9193	1.0501	0.1055
26	0.99	4.4479	0.9464	1.1063	0.0638
28	0.87	5.2538	0.9512	1.3277	0.0498
30	0.63	6.3473	0.9137	2.1566	0.1037
32	0.56	7.7496	0.9242	2.4552	0.0908
34	0.42	8.6566	0.9776	1.3673	0.0183
36	0.36	10.372	1.0131	0.3586	0.0056

[a] Refer to above experimental section for description of measurements; for both measurements concentration of polymer in water = 1.2×10^{-4} M (1.6 mg/mL) based on M_n 13,600 g/mol (^{1}H NMR estimate); refer to figure below for plotted result.

[b] A_0 refers to measured absorbance intensity at onset of thermal decolouration period

Table 8: Capture of SOX-PROP into micelles made from **5** $(BA)_{93}$-*b*-$(NAM)_{89.}$[a]

[Polymer] (mg/ml)	Polymer (mg)	D_h (nm) PDI	$t_{1/2}$ (s)	A_0[d]	k_1 (min^{-1})	A_1	k_2 (min^{-1})	A_2
0.24	1.1	-	6.4	1.83	6.8656	1.0313	0	0
0.61	2.8	-	5.6	1.31	7.7933	1.0309	0	0
1.21	5.5	52.5 (0.225)	4.6	1.29	9.2046	1.0042	0	0
1.95	8.9	48.6 (0.169)	4.3	1.32	10.4540	1.0491	0	0
4.21	19.2	43.3 (0.115)	3.8	1.25	11.5640	1.0363	0	0

Table 9: Decolouration kinetics of SOX-$(BA)_{135}$-*b*-$(NAM)_{104}$ block copolymer **6** in water *vs* DLS result.

[Polymer] (mg/ml)	Polymer (mg)	D_h (nm) PDI	$t_{1/2}$ (s)	A_0[b]	k_1 (min^{-1})	A_1	k_2 (min^{-1})	A_2
4.40	19.8	49.9 (0.113)	4.2	1.18	10.5420	1.0391	0	0

[a] Refer to experimental section for full description of procedure

[b] A_0 refers to measured absorbance intensity at onset of thermal decolouration period