Electronic Supplementary Information for Dalton Transactions

Using metal-ligand interactions for the synthesis of metallostar polymers

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Methods

^{1}H and ^{13}C NMR were 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) as internal reference. GPC data for uncomplexed polymers were obtained in THF (Shimadzu UFLC autosampler with Polymer Laboratories gel 5 μm Mixed C column) at room temperature with PMMA standards at a flow rate of 1 $mlmin^{-1}$ whilst the complexed polymers were run at a flow rate of 0.5 $mlmin^{-1}$ with 5 Mm NH_4PF_6 as an additive. All infrared spectra were collected on a Perkin Elmer Spectrum 100 FTIR ATR unit and UV studies were performed using a Perkin Elmer Lambda 35 UV/Vis spectrometer. FT-IR studies were conducted using Perkin Elmer Spectrum 100 FT-IR spectrometer and fluorescence studies were carried out using a Perkin Elmer LS 55 fluorescence spectrometer.

Hydrodynamic diameters (D_h) and size distributions of the assembles in aqueous solutions were determined by dynamic light scattering (DLS). The DLS instrumentation consisted of a Malvern Zetasizer Nano ZS instrument operating at 20 °C with a 4 mW He-Ne 633-nm laser module. Measurements were made at a detection angle of 173° (back scattering), and Malvern DTS 5.02 software was utilized to analyze the data. All determinations were made in triplicate. All elemental

analyses were performed by the Analytical Service in the Chemistry Department of the University of Cambridge.

Materials

AIBN (2,2'-Azobis(2-methylpropionitrile)) was recrystallized twice from methanol and stored in the dark at 4 °C. *Tert*-butyl acrylate, styrene and methyl methacrylate (MMA) 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-(Dodecylthiocarbonothioylthio)-2-methylpropanoic acid (DDMAT) and acid functionalised trithiocarbonate,[1] $Ru(DMSO)_4Cl_2$[2] and 3-azido-propan-1-ol[3] were synthesized according to literature methods.

Synthesis of 1

$Pd(PPh_3)_2Cl_2$ (210 mg, 0.299 mmol) was added under nitrogen to a Schlenk tube. Dry DMF (10 mL) and dry $^{i}Pr_2NH$ (10 mL) were then added using standard Schlenk techniques, followed by ethynyltrimethylsilane (1.067 mL, 742 mg, 7.55 mmol), CuI (78.34 mg, 0.412 mmol) and 2,6-dibromopyridine (886 mg, 3.74 mmol). The mixture was allowed to stir under nitrogen for 18h. The volatiles were then removed *in vacuo* and the crude product was washed with water (2x), extracted with CH_2Cl_2 (2x) dried over $MgSO_4$ and concentrated under reduced pressure. The brown solid obtained was purified by silica gel column chromatography, eluent 1:1 CH_2Cl_2:hexanes, to give **1a** as a yellow powder (88 % yield). Calc. for $C_{15}H_{21}NSi_2$: C, 66.42; H, 7.74; N, 5.16. Found: C, 66.15; H, 7.75; N, 5.18 %. ^{1}H-NMR ($CDCl_3$): δ, 7.49 (t, 1H, Ar-H), 7.30 (d, 2H, Ar-H), 0.18 (s, 18H, $-CH_3$). ^{13}C-NMR ($CDCl_3$): δ, 143.4, 136.3, 126.7 (pyridine), 103.1, 95.4 (-C≡C-), 0.3 ($-CH_3$).

To a solution of **1a** (930 mg, 3.4 mmol) in THF were added AcOH (408 mg, 6.8 mmol) and 2 mL of a TBAF 1M solution in THF. The reaction mixture was stirred at room temperature for 1 hour. The volatiles were then removed in vacuo and the crude product was purified by silica gel column chromatography (CH_2Cl_2:hexanes, 1:2) to afford **1b** in a 91 % yield. Calc. for C_9H_5N: C, 85.04; H, 3.93; N, 11.02. Found: C, 84.94; H, 4.05; N, 10.75 %. ^{1}H NMR ($CDCl_3$): δ = 7.62 (t, 1H, Ar-H), , 7.46 (d, 2H, Ar-H), 3.15 (s, 2H, C≡CH). ^{13}C NMR ($CDCl_3$): δ = 143.2, 135.3, 127.5 (pyridine), 86.3, 72.7 (-C≡C-).

A solution of 2,6-diethynylpyridine, **1b** (1 mmol, 127 mg), 3-azidopropan-1-ol[3] (2.2 mmol, 222 mg), sodium ascorbate (0.2 mmol, 44.6 mg), and $CuSO_4$ (0.02 mmol, 5.6 mg) in a 1:1 mixture of EtOH:H_2O (14 mL) was stirred at room temperature for 24 h. After removal of the solvents in vacuo, the crude product, was purified by column chromatography (CH_2Cl_2:MeOH, 3:1) to afford **1** (96 % yield). Calc. for $C_{15}H_{19}N_7O_2$: C, 54.70; H, 5.81; N, 29.77. Found: C, 54.57; H, 5.82; N, 29.46. ^{1}H NMR ($CDCl_3$), δ = 8.48 (s, 2H, N-CH=C-), 8.12 (d, 2H, Ar-H), 7.76 (t, 1H, Ar-H), 4.61 (t, 4H, O-CH_2), 3.62 (t,4H, N-CH_2-), 2.26 (m, 4H, CH_2-CH_2-CH_2). ^{13}C NMR ($CDCl_3$), δ = 152.4, 149.6, 139.5, 124.8, 120.1, 59.9, 48.9, 34.9. IR (KBr) = 3336, 3161, 3122, 2955, 2908, 2877, 1607, 1577, 1455, 1414, 1334, 1230, 1200, 1076, 1045, 812 cm^{-1}.

Synthesis of 2 - Route 1

To a solution of DDMAT[1] (670 mg, 1.84 mmol) was added EDCI.HCl (388 mg, 2 mmol), DMAP (22.5 mg, 0.184 mmol) and **1** (605 mg, 1.84 mmol) at room temperature. The reaction mixture was allowed to stir for 18 hours and the crude product was purified by column chromatography (EtOAc:hexanes, 1:10) to afford **2** as a yellow solid (74 % yield). Calc. for $C_{49}H_{79}N_7S_6O_4$: C, 57.59; H, 7.73; N, 9.59.

Found: C, 57.63; H, 7.78; N, 9.61 %. ^{1}H NMR ($CDCl_3$), δ = 8.32 (d, 2H, Ar-H), 8.20 (t, 1H, Ar-H), 7.59 (s, 2H, triazole-H), 4.43 (4H, t, N-C$\underline{H}_2$-), 4.13 (4H, t, -C(=O)-O-C$\underline{H}_2$), 3.22 (4H, t, S-C$\underline{H}_2$-$(CH_2)_9$-CH_3), 2.05 (m, 4H, CH_2-C$\underline{H}_2$-CH_2), 1.69 (12H, s, -$(CH_3)_2$), 1.4-1.2 (36H, m, S-CH_2-(C$\underline{H}_2$)$_9$-CH_3), 0.81 (6H, t, S-$(CH_2)_{10}$-C$\underline{H}_3$). ^{13}C NMR ($CDCl_3$), δ = 221.9 (C(=S)), 171.2 (C(=O)), 153.4 (py), 149.69 (py), 139.9 (py), 124.9 (C=C), 120.9 (C=C), 62.5 (-$\underline{C}H_2$-O-C(=O)), 48.7 (CH_2-$\underline{C}H_2$-CH_2-), 38.3 ($\underline{C}H_2$-S-), 37.8 (S-$\underline{C}H_2$-$(CH_2)_{10}$-), 34.3 (N-CH_2-), 32.3, 30.0, 29.7, 29.5, 29.4, 29.3, 28.5, 25.6 , 23.1 (CH_3-$\underline{C}H_2$-$(CH_2)_{10}$-S), 14.5 (S-$(CH_2)_{11}$-$\underline{C}H_3$).

Synthesis of 2 - Route 2

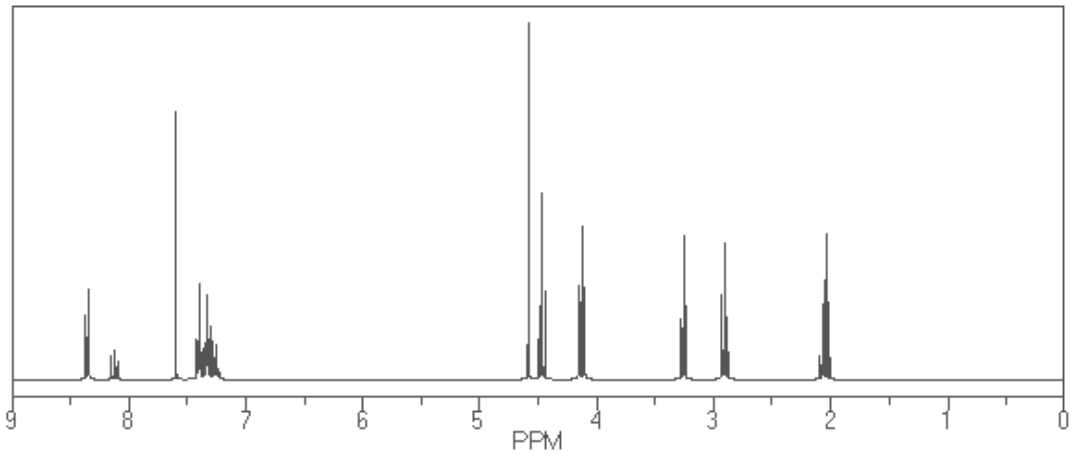
To a solution of DDMAT[1] (670 mg, 1.84 mmol) was added EDCI.HCl (388 mg, 2 mmol), DMAP (22.5 mg, 0.184 mmol) and 3-azido-propan-1-ol[3] (186 mg, 1.84 mmol) at room temperature. The reaction mixture was allowed to stir for 18 hours and the crude product was purified by column chromatography (EtOAc:hexanes, 1:10) to afford a yellow oil, **2a** (79 % yield). ^{1}H NMR ($CDCl_3$): δ = 4.17 (2H, t, -CH_2-C$\underline{H}_2$-O-C=O), 3.35 (2H, t, -CH_2-C$\underline{H}_2$-N_3), 3.27 (2H, t, -CH_2-C$\underline{H}_2$-S-(C=S)), 1.89 (2H, t, -C$\underline{H}_2$-CH_2-N_3), 1.72-1.61 (8H, m, -C$\underline{H}_2$-CH_2-S-(C=S), -S-C(C$\underline{H}_3$)$_2$-(C=O)), 1.38-1.25 (18H, m, CH_3-(C$\underline{H}_2$)$_9$-CH_2-CH_2S-C=S), 0.87 (3H, t, C$\underline{H}_3$-C_9H_{18}-CH_2-CH_2-S-). ^{13}C NMR ($CDCl_3$): δ = 222.6 (C=S), 172.7 (C=O), 62.6 (-CH_2-$\underline{C}H_2$-O-C=O), 55.8 (-S-$\underline{C}(CH_3)_2$-(C=O)), 48.1 (-CH_2-$\underline{C}H_2$-N_3), 36.8 (-CH_2-$\underline{C}H_2$-S-), 31.8 (-$\underline{C}H_2$-CH_2-N_3), 29.6, 29.5, 29.4, 29.3, 29.0, 28.9, 27.9, 27.8, 25.2 (-S-C($\underline{C}H_3$)$_2$-(C=O)), 22.6 (-$\underline{C}H_2$-CH_2-S), 14.0 ($\underline{C}H_3$-C_9H_{18}-CH_2-CH_2-S-(C=S)). IR ν = 2923, 2853, 2097, 1735, 1465, 1382, 1364, 1257, 1155, 1124, 1065, 870 cm^{-1}. To a solution of azido-functionalised RAFT agent, **2a** (229 mg, 0.64 mmol) in dry THF were added CuBr (23.1 mg, 0.16 mmol), PMDETA (27.9 mg, 2.31 μL, 0.16 mmol) and 2,6-diethynylpyridine **1b** (40

mg, 0.32 mmol) and the reaction mixture was stirred at room temperature for 8 hours. The volatiles were then removed in vacuo and the crude product was purified by column chromatography (EtOAc:hexanes, 1:5, 3 % Et_3N) to afford **2** as a yellow solid (92 % yield). Characterisation data was identical for CTA **2** produced by route 1.

Synthesis of 3

To a solution of acid functionalised trithiocarbonate[1] (500 mg, 1.84 mmol) was added EDCI.HCl (388 mg, 2 mmol), DMAP (22.5 mg, 0.184 mmol) and **1** (605 mg, 1.84 mmol) at room temperature. The reaction mixture was allowed to stir for 18 hours and the crude product was purified by column chromatography (EtOAc:hexanes, 1:10) to afford **3** as a yellow solid (overall 57 % yield). Calc for $C_{35}H_{39}N_7S_6O_4$: C, 51.66; H, 4.97; N, 12.05. Found: C, 51.74; H, 4.90; N, 12.20 %. ^{1}H NMR δ = 8.16 (s, 2H, triazole-H), 8.08 (d, 2H, Ar-H), 7.74 (t, 1H, Ar-H), 7.29-7-33 (10H, m, Ph-H), 4.61 (4H, s, C$\underline{H}_2$-Ph), 4.46 (4H, t, C$\underline{H}_2$-N_3), 4.13 (4H, t, -C$\underline{H}_2$-O), 3.26 (4H, t, CH_2-C$\underline{H}_2$-S), 2.79 (4H, t, C$\underline{H}_2$-CH_2-S), 2.05 (4H, quint, CH_2-C$\underline{H}_2$-CH_2). ^{13}C NMR ($CDCl_3$): δ = 220.8 (C(=S)), 169.8 (C(=O)), 152.3 (py), 149.1 (py), 139.5 (py), 135.2 (Ph), 129.8 (Ph), 129.6 (Ph), 128.7 (Ph), 124.2 (C=C), 120.7 (C=C), 62.8 (-$\underline{C}H_2$-O-C(=O)), 48.5 (CH_2-$\underline{C}H_2$-CH_2-), 34.6 (N-CH_2-).

^{1}H NMR spectrum of 3 in $CDCl_3$.



General polymerisation procedures

Monomer (10 mmol), CTA (0.05 mmol), and AIBN (0.01 mmol) were dissolved in dioxane (1:1 v/v). 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 the required temperature 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 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 yellow coloured polymer.

Representative complexation procedure for 2

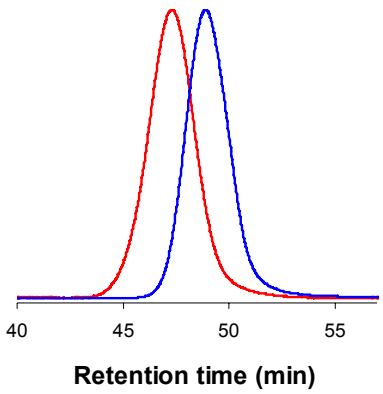
[Ru(**2**)$_2$]•2PF_6 : The CTA **2** (21 mg, 0.21 mmol) in 10 mL ethylene glycol was added to the ruthenium(II) precursor $Ru(DMSO)_4Cl_2$[3] (0.1 mmol, 46 mg) in 4 mL of MeOH:H_2O in a 1:1.05 ratio. The mixture was heated under N_2 at 100 ^oC for 4 h, producing a yellow solution, which was then cooled to room temperature. Water was

added to reach a total volume of 36 mL and solid NH_4PF_6 was added whereupon a yellow precipitate formed. The precipitate was washed thoroughly with H_2O and dried under vacuum. (87 mg, 92% yield).

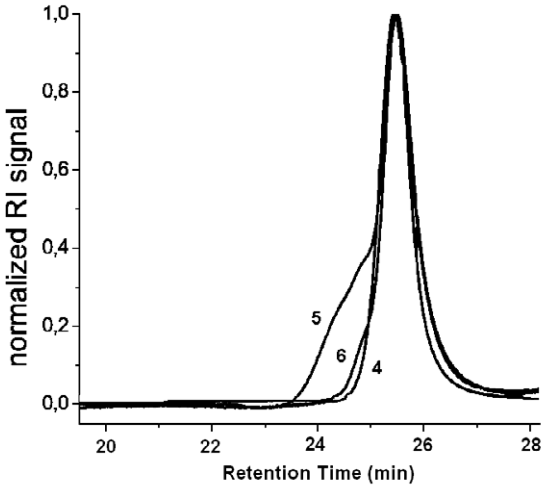
Representative complexation procedure for 4

The polymer **4** (M_n = 13,600, M_w/M_n = 1.13) in 5 mL DMSO was added to the ruthenium(II) precursor $Ru(DMSO)_4Cl_2$[3] in 2 mL DMSO in a 1:2 ratio. The mixture was heated under N_2 at 100 ^oC for 4 h, producing a yellow solution, which was then cooled to room temperature. Water was added to reach a total volume of 30 mL and solid NH_4PF_6 was added whereupon a yellow precipitate formed. The precipitate was washed thoroughly with H_2O and MeOH and dried under vacuum.

GPC trace of polymer PtBuA-*b*-PS (red trace) and PS (blue trace) from CTA 2 in THF (Table 1 entry 6 upon chain extension of entry 2)

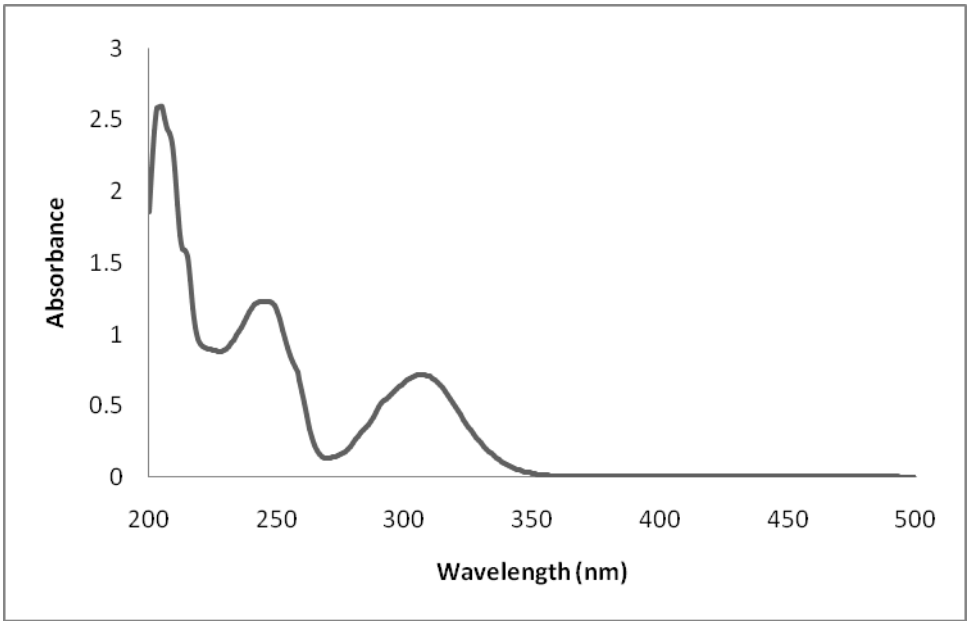


GPC trace of polymer of 4, 5 and 6 in THF (with added NH_4PF_6)

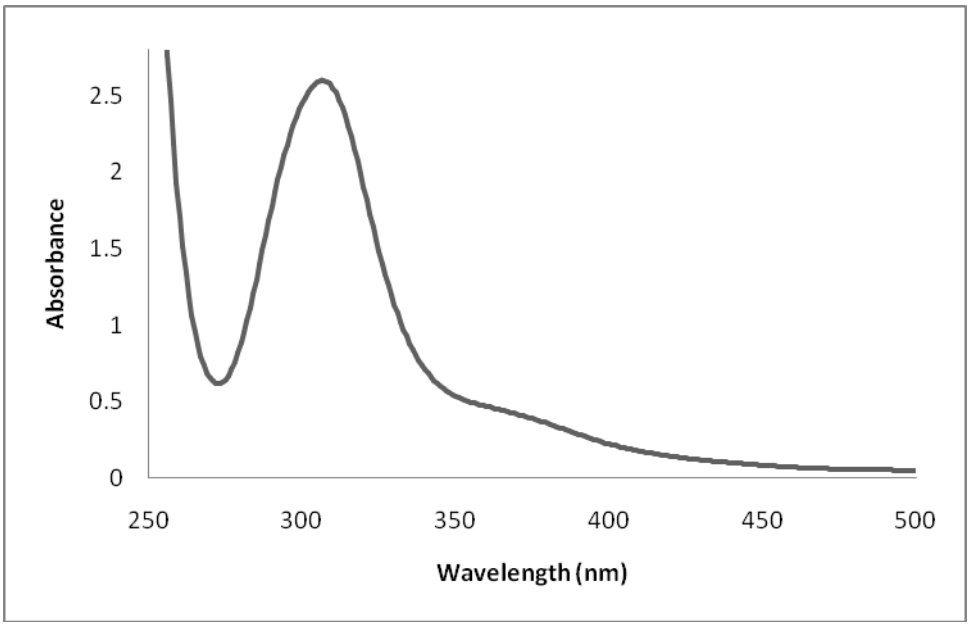


UV-vis spectrum of RAFT agent 2 (in MeCN)

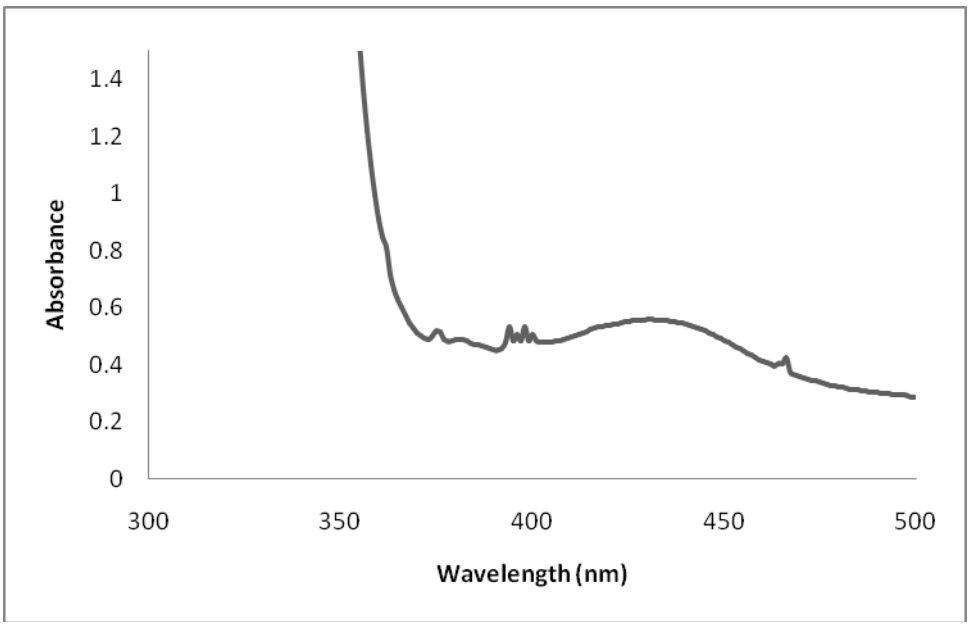
Characteristic trithiocarbonate absorbance at *ca.* 310 nm



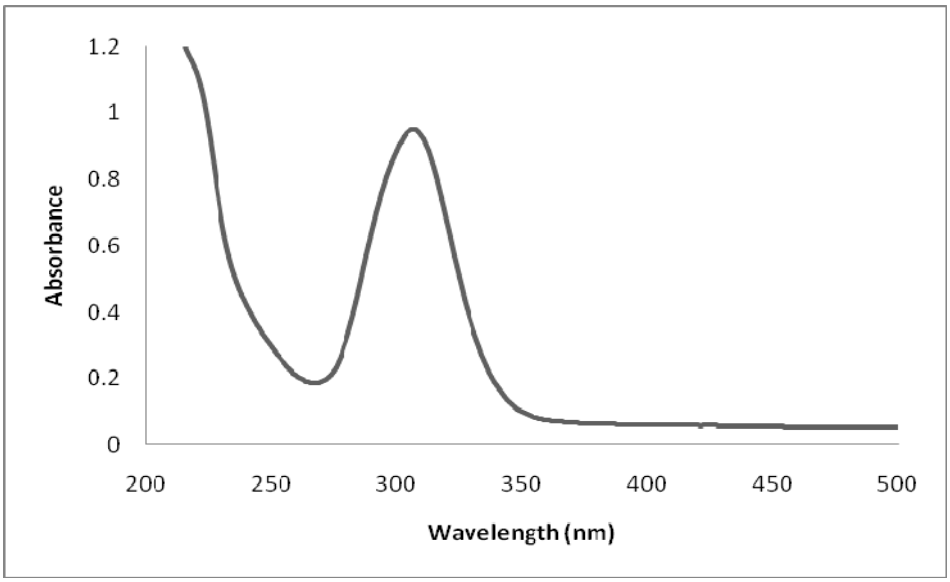
With Ru(II) in MeCN – λ_{max} *ca.* 390 nm



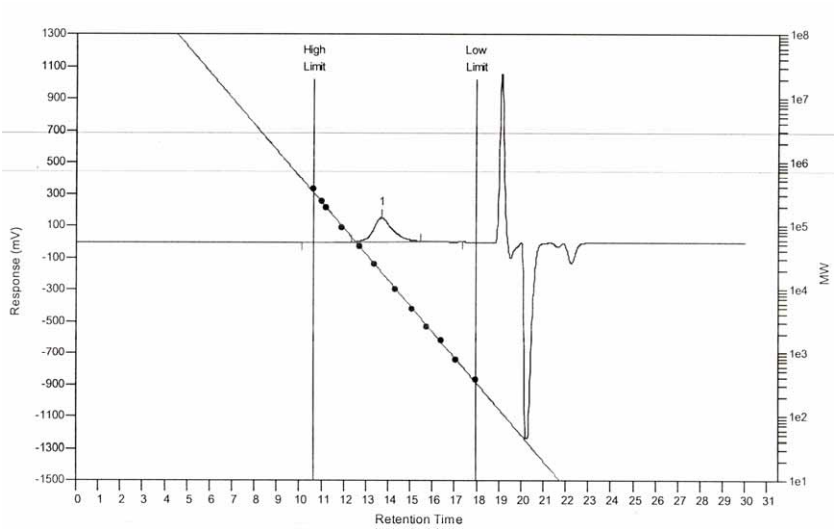
With Fe(II) in MeCN - λ_{max} *ca.* 440 nm (note due to the high extinction coefficient of the SSS group, it is very difficult to clearly see both absorbances in a single spectra)



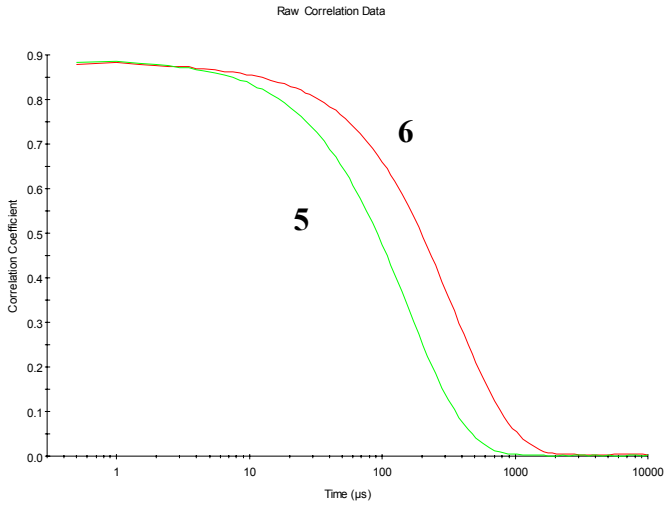
With Eu(III) in MeCN - λ_{max} expected *ca.* 306 nm but masked by trithiocarbonate absorbance



GPC trace of polymer 4



DLS correlation functions of 5 and 6



References

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3. A.J. Scheel, H. Komber and B.I. Voit, *Macromol. Rapid Commun*. 2004, *25*, 1175.