

Electronic Supplementary Information

RAFT Polymerization of Luminescent Organoboron 8-Hydroxyquinolate Monomers

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Experimental Methods

Materials and General Methods. mPEG ($M_n = 2000$, $\eta = 45$; $PDI = 1.04$) was purchased from Aldrich, mPEO ($M_n = 19300$, $\eta = 440$; $PDI = 1.03$) was purchased from Polymer Source Inc., and BBr_3 (99.9%), 8-hydroxyquinoline (99%), from Acros. **Caution!** BBr_3 is toxic and corrosive and should be handled appropriately with great care; fluorinated grease was used for ground glass joints in reactions involving boron tribromide. All chemicals were used as received without further purification. The RAFT agent mPEG-BSPA (BSPA=3-benzylsulfanylthiocarbonylsulfanylpropionic acid),¹ 4-trimethylsilyl-1-*t*-butylbenzene² and 4-trimethylstannylstyrene³ were prepared according to literature procedures. Reactions and manipulations involving reactive boron species were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (Innovative Technologies). Ether solvents were distilled from Na/benzophenone prior to use. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies; alumina/copper columns for hydrocarbon solvents); chlorinated solvents were subsequently distilled from CaH_2 and degassed via several freeze-pump-thaw cycles.

The 499.9 MHz 1H and 125.7 MHz ^{13}C NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer. The 160.4 MHz ^{11}B NMR spectra were recorded with a boron-free probe using boron-free quartz NMR tubes. 1H and ^{13}C NMR spectra were referenced internally to the solvent peaks and the ^{11}B NMR spectra externally to $BF_3 \cdot Et_2O$ ($\delta = 0$) in C_6D_6 . Elemental analyses were performed by Quantitative Technologies Inc. Whitehouse, NJ.

GPC analyses were performed in THF (1 mL/min) or THF/2vol% NEt_3 using a Waters Empower system equipped with a 717plus autosampler, a 1525 binary HPLC pump, a 2487 dual λ absorbance detector, and a 2414 refractive index detector. Two styragel columns (Polymer Laboratories; 5 μm Mix-C), which were kept in a column heater at 35 $^\circ C$, were used for separation. The columns were calibrated with polystyrene standards (Polymer Laboratories). Multiangle laser light scattering (MALLS) experiments were performed at 690 nm (30 mW linear polarized GaAs laser) using a Wyatt Dawn EOS instrument in-line with the GPC; a Wyatt Optilab refractive index detector operated at 690 nm was used as the concentration detector for in-line GPC-MALLS measurements.

Dynamic light scattering (DLS) studies were performed using the Wyatt Dawn EOS modified with a Wyatt QELS attachment. Data were collected at an angle of 108 $^\circ$ using an avalanche photodiode and an optical fiber and processed with the Wyatt QELS software (regularization analysis with DYNALS algorithm, intensity-weighted average hydrodynamic radius).

UV-visible absorption data were acquired on a Varian Cary 500 UV-Vis / NIR spectrophotometer. The fluorescence data and quantum yields were measured on a Varian Cary Eclipse Fluorescence spectrophotometer with optically dilute solutions ($A < 0.1$). Anthracene was used as the standard and the quantum yield of anthracene ($\Phi = 0.33$) was adopted from the Handbook of Photochemistry⁴. Sample solutions were prepared using a microbalance (± 0.1 mg) and volumetric glassware. The quantum yield was calculated by plotting a graph of integrated fluorescence intensity vs. absorbance of at least 4 solutions with increasing concentration. The

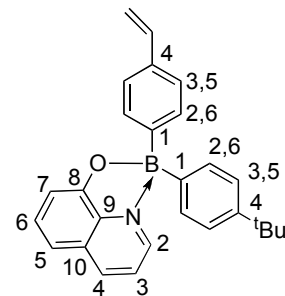
gradient of the graph is proportional to the quantum yield. The formula used to calculate the absolute quantum yield is $\Phi = \Phi_{\text{standard}} \times \text{Gradient}_{\text{compound}} / \text{Gradient}_{\text{standard}}$.

Fluorescence images were obtained on a Zeiss LSM 510 confocal microscope, utilizing a 63x / 1.4 numerical aperture Plan Apochromat oil objective (Carl Zeiss, Jena, Germany). The excitation wavelength was 458 nm, and a BP 500-550 IR filter was applied for fluorescence detection.

Experimental Procedures

Synthesis of 4-Styryl-4-*t*-butylphenylboron Quinolate Monomer

M1. To a solution of boron tribromide (2.07 g, 8.62 mmol) in anhydrous toluene (10 mL) was added dropwise under stirring a solution of 1-trimethylsilyl-4-*tert*-butylbenzene (1.43 g, 6.90 mmol) in toluene (10 mL) at RT. The mixture was stirred at RT overnight, all volatile components were removed under high vacuum and the residue was redissolved in CH₂Cl₂ (10 mL). Then, a solution of 4-trimethylstannylstyrene (1.84 g, 6.90 mmol) in CH₂Cl₂ (10 mL) was added slowly under stirring. After 2 h, a solution of 8-methoxyquinoline (1.10 g, 6.91 mmol) in CH₂Cl₂ (10 mL) was added dropwise and the mixture was stirred for an additional hour. The reaction mixture was extracted with 3 x 50 mL of aqueous ammonium bicarbonate (10%) and the combined organic layers were dried over sodium sulfate. After rotary evaporation, the crude product was recrystallized from CH₂Cl₂/ether solvent mixture (v/v=1/2), to give **M1** as a yellow microcrystalline solid. Yield: 2.0 g, 74%. ¹H NMR (499.895 MHz, CDCl₃): δ = 8.60 (d, ³J = 5.0 Hz, 1H, Q-H2), 8.40 (d, ³J = 8.5 Hz, 1H, Q-H4), 7.66 (pst, ³J = 8.0 Hz, 1H, Q-H6), 7.62 (dd, ³J = 5.0 Hz and 8.5 Hz, 1H, Q-H3), 7.46 (d, ³J = 7.5 Hz, 2H, Ph-H2,6), 7.37 (d, ³J = 8.0 Hz, 2H, Sty-H2,6), 7.33 (d, ³J = 8.0 Hz, 2H, Ph-H3,5), 7.33 (d, ³J = 8.5 Hz, 2H, Sty-H3,5), 7.24 (d, ³J = 8.0 Hz, 1H, Q-H5), 7.18 (d, ³J = 7.5 Hz, 1H, Q-H7), 6.70 (dd, ³J = 11.0, 17.5 Hz, 1H, Vi), 5.70 (d, ³J = 17.5 Hz, 1H, Vi), 5.16 (d, ³J = 11.0 Hz, 1H, Vi), 1.30 (s, 9H, CMe₃); ¹³C NMR (125.698 MHz, CDCl₃): δ = 159.1 (Q-C8), 149.8 (Ph-C4), 143.8 (br., Ph-C1), 139.5 (Q-C2/4), 138.8 (Q-C2/4), 137.9 (Q-C9), 137.5 (vinyl-C), 136.4 (styryl-C4), 133.1 (Q-C6), 132.4 (styryl-C2,6), 132.0 (Ph-C2,6), 128.7 (Q-C10), 125.7 (styryl-C3,5), 124.7 (Ph-C3,5), 122.9 (Q-C3), 113.0 (vinyl-C), 112.3 (Q-C5), 109.9 (Q-C7), 34.6 (CMe₃), 31.6 (CMe₃), styryl-C1 not observed; ¹¹B NMR (160.386 MHz, CDCl₃) δ = 11.4 (w_{1/2} = 400 Hz). Elemental analysis for C₂₇H₂₆BNO: calcd C 82.87, H 6.70, N 3.58; found C 82.60, H 6.75, N 3.49%.



Synthesis of M2. To a solution of boron tribromide (1.62 g, 6.47 mmol), in 10 mL of anhydrous toluene was added dropwise of a solution of 1-trimethylsilyl-4-*tert*-butylbenzene (0.89 g, 4.31 mmol) in 10 mL anhydrous toluene at RT under stirring. The mixture was stirred overnight, followed by removing the excess boron tribromide and toluene under high vacuum. The residue was redissolved in 10 mL of dry CH₂Cl₂. Then, a solution of 4-trimethylstannylstyrene (1.15 g, 4.31 mmol) in CH₂Cl₂ (10 mL) was added dropwise under stirring. After 2 h, a solution of 5-(4'-dimethylamino phenyl)-8-methoxyquinoline (1.20 g, 4.31 mmol) in CH₂Cl₂ (25 mL) was added dropwise and the mixture was stirred for another 2 h. The reaction mixture was worked up with 3x50 mL of aqueous ammonium bicarbonate (10%), and the combined organic layers were dried over sodium sulfate. After rotary evaporation, the crude monomer was purified by column chromatography on silica gel with CH₂Cl₂ as the eluent.

Recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexanes}=1/2$ (v/v) mixture gave **M2** as an orange microcrystalline solid. Yield: 1.80 g, 82%. ^1H NMR (499.895 MHz, CDCl_3): δ = 8.60 (d, 3J = 4.0 Hz, 1H, Q-H2), 8.59 (overlapped, 1H, Q-H4), 7.62 (d, 3J = 8.0 Hz, 1H, Q-H6), 7.57 (dd, 3J = 5.0 Hz and 8.0 Hz, 1H, Q-H3), 7.51 (d, 3J = 8.0 Hz, 2H, styryl-H2,6), 7.44 (d, 3J = 8.0 Hz, 2H, Ph-H2,6), 7.4-7.3 (m, 6H, ^oPh -H3,5, Ph-H3,5, styryl-H3,5), 7.22 (d, 3J = 8.0 Hz, 2H, Q-H7), 6.89 (d, 3J = 8.5 Hz, 2H, ^oPh -H2,6), 6.72 (dd, 3J = 11.0, 17.5 Hz, 1H, Vi), 5.72 (d, 3J = 17.5 Hz, 1H, Vi), 5.18 (d, 3J = 11.0 Hz, 1H, Vi), 3.05 (s, 6H, NMe_2), 1.32 (s, 9H, CMe_3); ^{13}C NMR (125.698 MHz, CDCl_3): δ = 157.7 (Q-C8), 150.1 (^oPh -C1), 149.7 (Ph-C4), 139.3 (Q-C2/4), 138.3 (Q-C2/4), 138.0 (Q-C9), 137.6 (vinyl-C), 136.3 (styryl-C4), 132.6 (Q-C6), 132.5 (styryl-C2,6), 132.0 (Ph-C2,6), 130.5 (^oPh -C3,5), 127.2 (Q-C10), 126.8 (Q-C5), 126.2 (^oPh -C4), 125.7 (styryl-C3,5), 124.7 (Ph-C3,5), 122.6 (Q-C3), 113.0 (vinyl-C), 112.9 (^oPh -C2,6), 109.9 (Q-C7), 40.8 (NMe_2), 34.6 (CMe_3), 31.6 (CMe_3), n.o. (Ph-C1, styryl-C1); ^{11}B NMR (160.386 MHz, CDCl_3) δ = 11.4 ($w_{1/2}$ = 400 Hz). Elemental analysis for $\text{C}_{35}\text{H}_{35}\text{BN}_2\text{O} \times 0.5(\text{C}_6\text{H}_{14})$: calcd C 82.45, H 7.65, N 5.06; found C 82.01, H 7.81, N 4.97%. The amount of cocrystallized hexanes was independently confirmed by ^1H NMR integration.

Example for the Synthesis of P1. A Schlenk tube was filled with methyl 3-benzylsulfanylthiocarbonylsulfanylpropionate (**CTA1**) (11.0 mg, 0.0384 mmol), **M1** (500 mg, 1.28 mmol), AIBN (2.1 mg, 0.0128 mmol in 2 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C. To determine the conversion of monomer at different times, one drop of solution was taken out with a syringe at 30 min, 75 min, 150 min, 270 min and 360 min for ^1H NMR analysis (the integral ratio of the vinyl signal at 5.16 ppm and the methyl group of anisole at 3.86 ppm was used to determine the monomer conversion). The polymerization was quenched at liquid nitrogen temperature after 360 min. The polymer was purified by two precipitations into a 10-fold volume of methanol and then dried under high vacuum. GPC-RI (THF, 1 mL/min): M_n = 5840, M_w = 7090, PDI = 1.21. The NMR data of **P1** were in good agreement with those reported for the polymer prepared by post-modification procedures,⁵ and no indication of different tacticity was found based on comparison of the ^{13}C NMR spectra.

Example for the Synthesis of P2. A Schlenk tube was filled with methyl 3-benzylsulfanylthiocarbonylsulfanylpropionate (**CTA1**) (6.73 mg, 0.0235 mmol), **M2** (600 mg, 1.18 mmol), AIBN (1.29 mg, 0.00784 mmol in 2 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C. After 9 h, the polymerization was quenched at liquid nitrogen temperature. The polymer was purified by 2 precipitations into a 10-fold volume of hexanes/methanol=2/1 (v/v) and then dried under high vacuum. The conversion of monomer based on the weight of the final product (350 mg) was determined to be 58%. GPC-RI (THF, 1 mL/min): M_n = 5220, M_w = 6550, PDI = 1.25. The NMR data of **P2** were in good agreement with those reported for the polymer prepared by post-modification procedures,⁵ and no indication of different tacticity was found based on comparison of the ^{13}C NMR spectra.

A similar procedure was used for a kinetic study, the results of which are given in Table 1 in the manuscript and illustrated in Figure S1 of the electronic supplementary information (ESI).

Kinetic analysis of the chain extension of CTA2 with M1. A flame-dried Schlenk tube was filled with **CTA2** (45 mg, 0.020 mmol), **M1** (780 mg, 2.00 mmol), AIBN (2.6 mg, 0.016 mmol in 3 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C and samples were withdrawn at predetermined times. Data from a kinetic analysis are provided in Figure S2.

Synthesis of P1-b-PEO(440). A flame-dried Schlenk tube was filled with **CTA3** (360 mg, 0.0184 mmol), AIBN (1.0 mg, 0.0061 mmol), **M1** (720 mg, 1.84 mmol in 4 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C. After 24 h, the polymerization was quenched at liquid nitrogen temperature. The polymer was purified by two precipitations into a 10-fold volume of cold ether and then dried under high vacuum. The isolated yield of the block copolymer was 0.60 g. The conversion of monomer based on the weight of the final product was determined to be ca. 33%. Elemental analysis for $C_7H_7(C_{27}H_{26}BNO)_{37}C_4H_4S_3O(C_2H_4O)_{440}OCH_3$: calcd C 66.51, H 8.07, N 1.51; found C 66.68, H 7.64, N 1.55%.

Synthesis of P2-b-PEO(440). A flame-dried Schlenk tube was filled with **CTA3** (391 mg, 0.020 mmol), AIBN (1.1 mg, 0.0067 mmol), **M2** (510.5 mg, 1.00 mmol in 2 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C. After 24 h, the polymerization was quenched at liquid nitrogen temperature. The polymer was purified by two precipitations into a 10-fold volume of cold ether and then dried under high vacuum. The isolated yield of the block copolymer was 0.57 g. The conversion of monomer based on the weight of the final product was determined to be ca. 35%. Elemental analysis for $C_7H_7(C_{35}H_{35}BN_2O)_{14}C_4H_4S_3O(C_2H_4O)_{440}OCH_3$: calcd C 61.91, H 8.51, N 1.46; found C 61.61, H 8.60, N 1.45%.

Aqueous Self-assembly of Block Copolymers. The block copolymer under investigation (2.5 mg) was dissolved in THF as a common solvent (5.0 mL), and deionized water was added dropwise under magnetic stirring. The final concentration of the polymer was 0.01 mg/mL. Then, the solution was dialyzed against deionized water for 3 days to remove THF (the water was replaced >5 times over this period).

References

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4. S. L. Murov, I. Carmichael and G. L. Hug, eds., *Handbook of Photochemistry*, Marcel Dekker Inc., New York, 1993.
5. Y. Qin, I. Kiburu, S. Shah and F. Jäkle, *Macromolecules*, 2006, **39**, 9041-9048.

Fig. S1. (A) Kinetic plot for the polymerization of **M2** (344 mg) in anisole (1 mL) at 80 °C; [M1]:[CTA1]:[AIBN]=33:1:0.33; (B) plot of M_n (from GPC vs. PS standards) vs. monomer conversion as determined by ^1H NMR integration (vinyl signal of **M2** vs anisole methyl group); (C) GPC curves for the polymerization of **M2**.

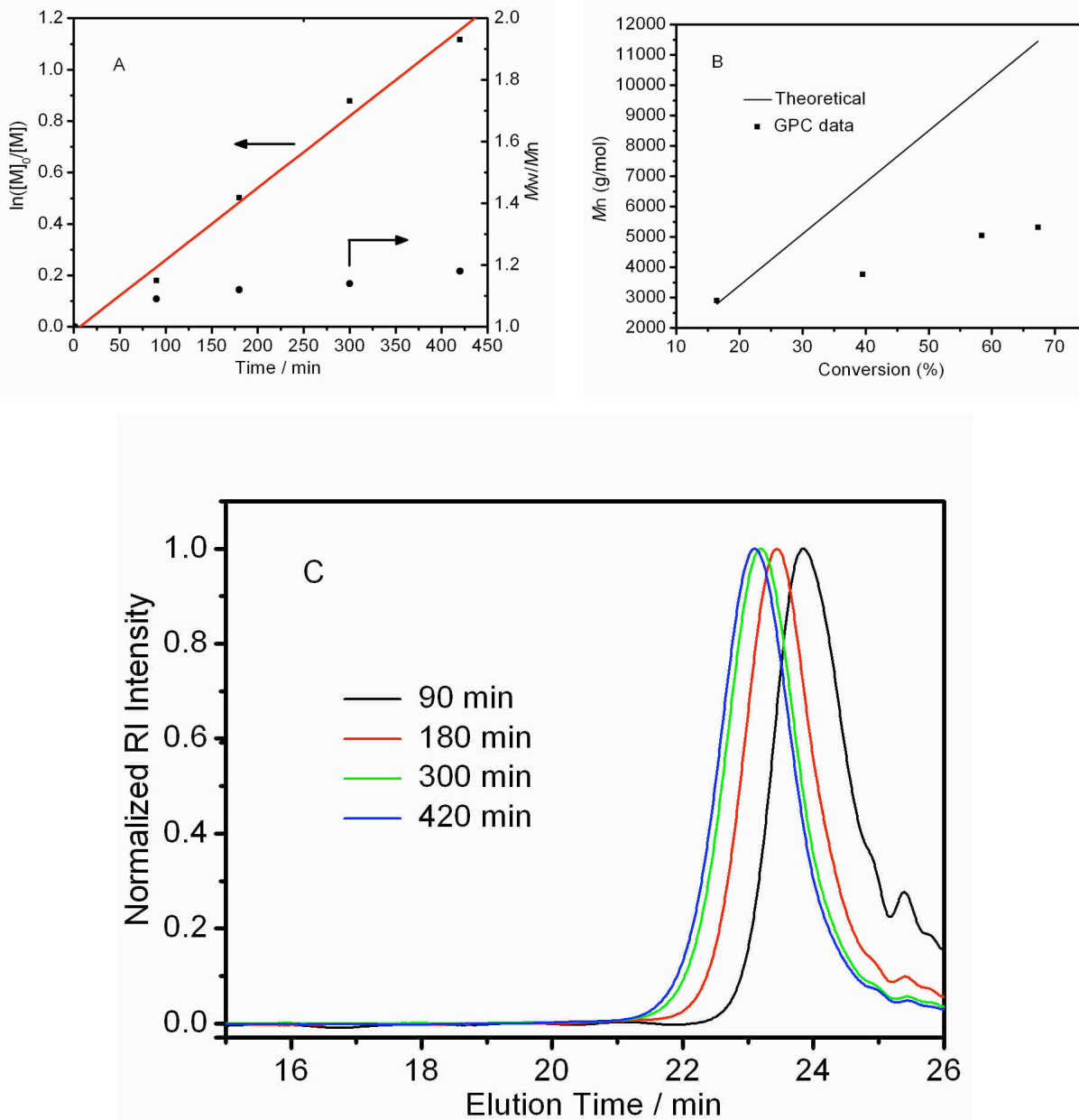


Fig. S2. (A) Kinetic plot for the chain extension of **CTA2** with **M1** (780 mg) in anisole (3 mL) at 80 °C; molar ratio of **[M1]:[CTA2]:[AIBN]**=100:1:0.8; (B) plot of M_n (from GPC vs. PS standards) vs. monomer conversion as determined by ^1H NMR integration (vinyl signal of **M1** vs anisole methyl group); (C) GPC curves for the chain extension of PEO with **M1**.

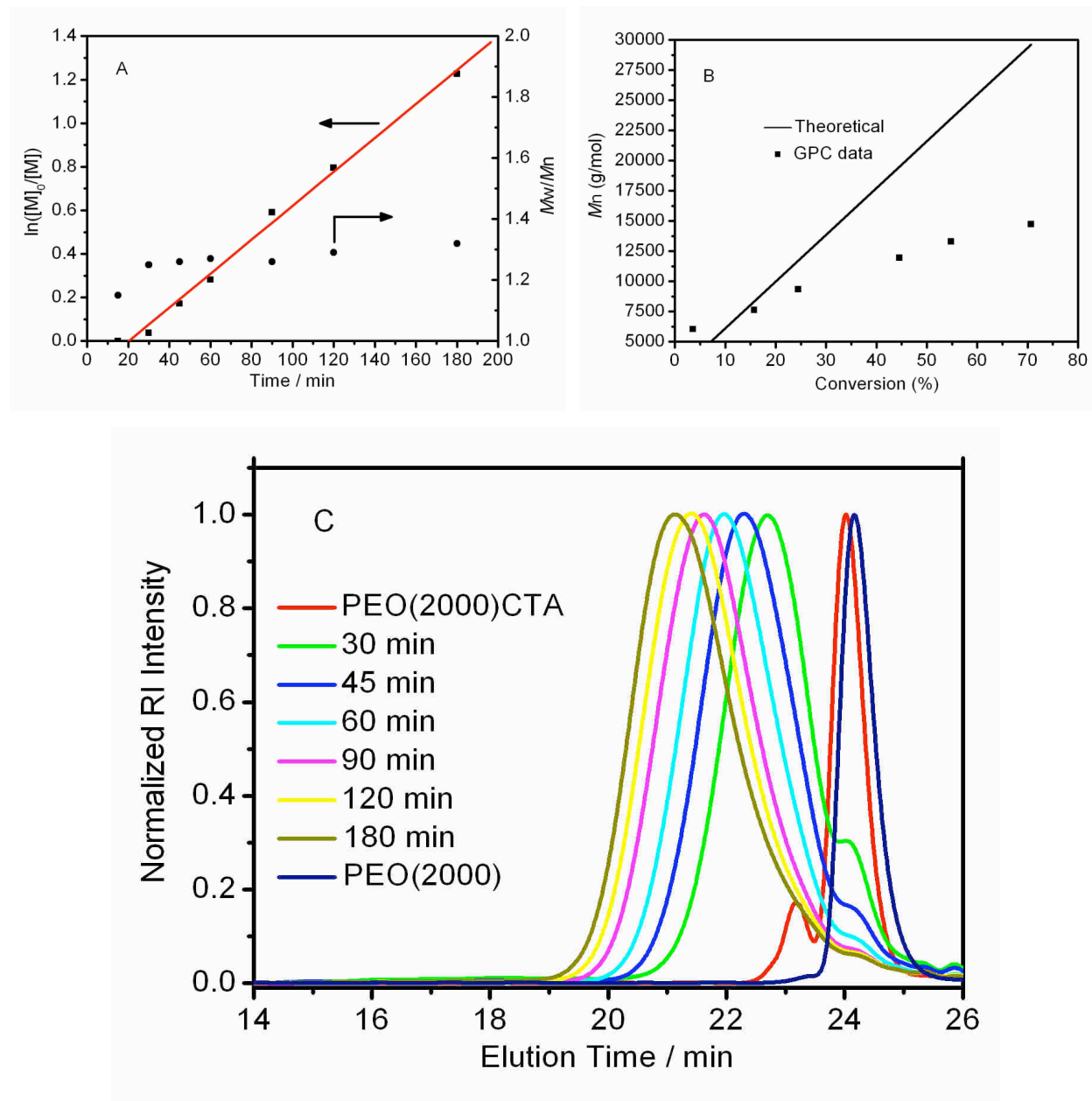


Fig. S3. ^1H NMR spectra of P1, P2, P1-b-PEO(440) and P2-b-PEO(440) in CDCl_3

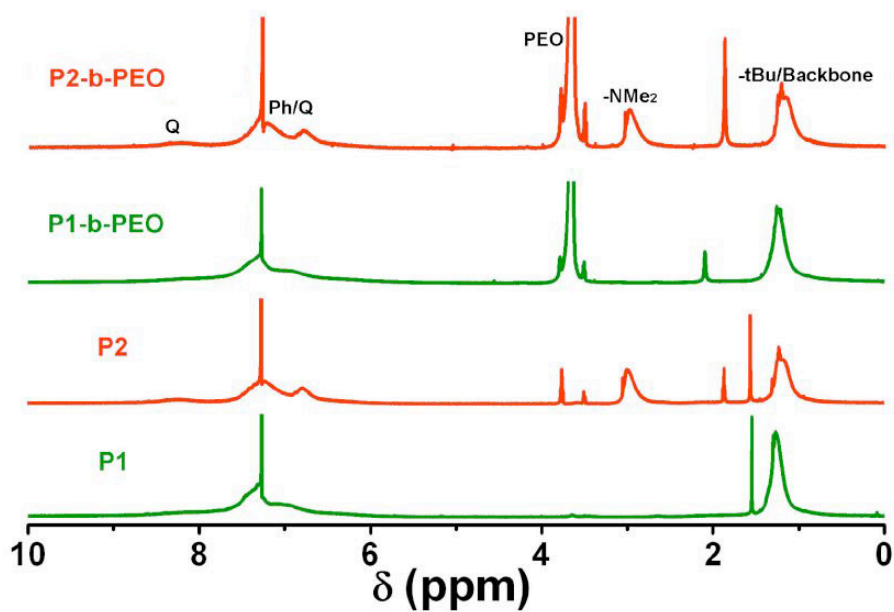


Fig. S4. ^{11}B and ^{13}C NMR spectra of the block copolymer P1-b-PEO(440) and comparison to the ^{13}C NMR of M1 monomer

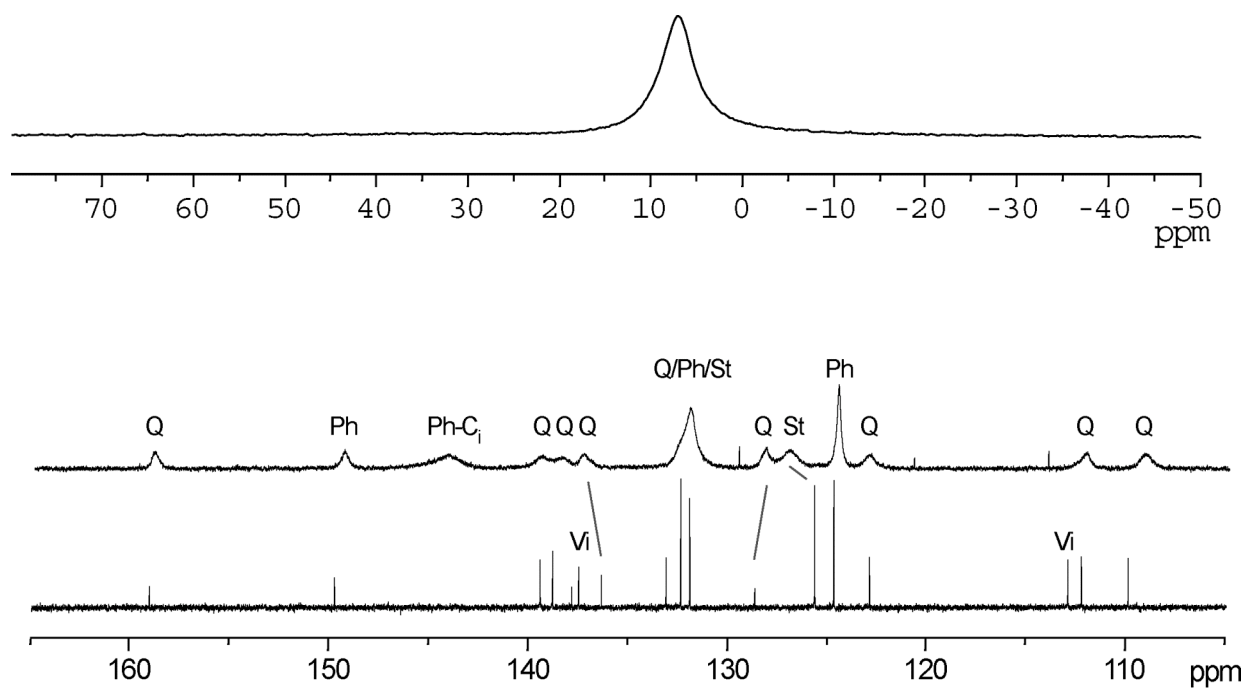


Fig. S5. UV-Vis and fluorescence spectra in THF (for M1, P1, P1-b-PEO(440) $\lambda_{exc} = 395$ nm; for M2, P2, P2-b-PEO(440) $\lambda_{exc} = 506$ nm)

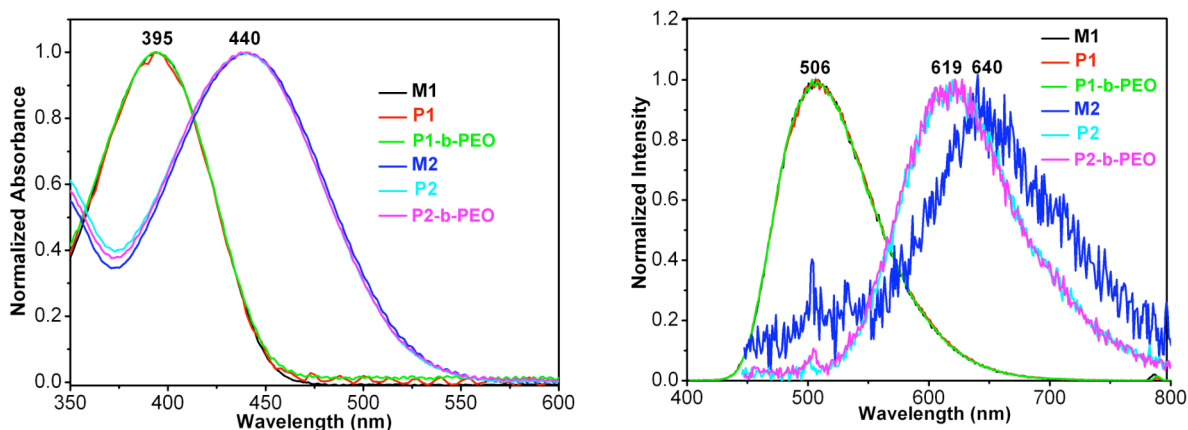


Table S1. Photophysical data of monomers and polymers in THF solution

Sample	M1	P1	P1-b-PEO(440)	M2	P2	P2-b-PEO(440)
λ_{abs} (nm)	395	395	395 (391 in H ₂ O)	440	440	440 (440 in H ₂ O)
ϵ (cm ⁻¹ M ⁻¹)	3370			3650		
λ_{em} (nm)	506	506	506 (503 in H ₂ O)	640	619	619 (621 in H ₂ O)
Φ_{Fl} (%)	20	15	20	0.03	0.2	0.2

Fig. S6. Fluorescence microscopy image (10 μ m \times 10 μ m) of an aqueous solution of P1-b-PEO(440) drop-cast onto a plastic substrate; $\lambda_{exc} = 450$ nm, detected at $\lambda = 500$ -550 nm. Spot size is diffraction-limited and shows correct particle location but not dimensions.

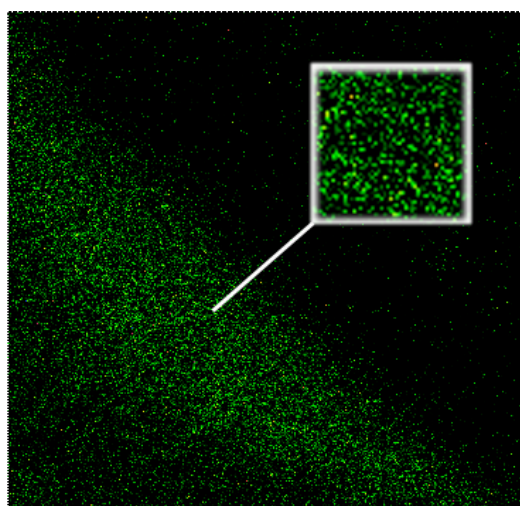


Fig. S7. DLS correlation functions for solutions of P1-b-PEO(440) and P2-b-PEO(440) in water

