Supporting Information

Mechanical stability of *cis, trans* - poly(*p*-phenylene vinylenes)

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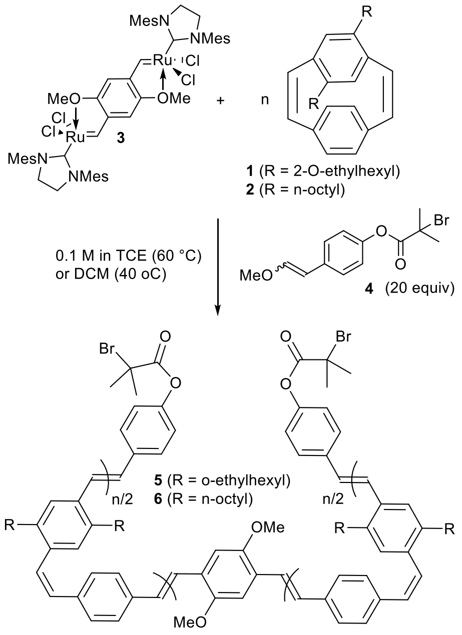
Table of Contents

S1. General experimental details 1
S2. ROMP of monomers **1** and **2** with catalyst **3** 2
S3. Synthesis of coil-rod-coil triblock copolymers 3
S4. General procedure for sonication 4
S5. General procedure for isomerisation 4
S6. Computational details 4
S7. CoGEF simulations results 5
S8. SEC traces 13
S9.Optical properties 15
S10. References 17

S1. General experimental details

Monomers **1** and **2** were synthesised by an established procedure developed in our laboratory.[1,2] All reagents were purchased from Sigma-Aldrich, Fisher Scientific, Alfa Aesar or Acros and used as received. Column chromatography was performed using silica gel (60 Å, 230−400 mesh). All reactions were carried out using standard Schlenk techniques under argon, unless stated otherwise. Degassed solvents were prepared either by purging with argon/nitrogen or by freeze-pump-thaw (three times). For ATRP; methyl methacrylate was passed through a short cesium carbonate and degassed by three freeze-pump-thaw cycles. NMR spectroscopic characterization was conducted on 500 MHz Brucker spectrometers using CD_2Cl_2 unless otherwise indicated. Chemical shifts are reported in ppm relative to the indicated residual solvent (^1H NMR spectroscopy; 5.23 ppm for dichloromethane-d_2). Gel permeation chromatography (GPC) analyses were performed in THF solution (~1 mg mL^{-1}) at 40 °C using a GPC Agilent 1260 Infinity II with 2 × PL gel 10 µm mixed-B and a PL gel 500 Å column, and equipped with a differential refractive index (DRI) detector employing narrow polydispersity polystyrene standards (Agilent Technologies) as a calibration reference. Samples were filtered through a Whatman Puradisc 4 mm syringe filter with 0.45 µm PTFE membrane before injection to equipment, and experiments were carried out with injection volume of 50 µL, flow rate of 1 mL min^{-1}. Results were analysed using Agilent GPC/SEC Software Version 2.2. The analysed samples contained *n*-dodecane as a flow marker. UV-visible absorption spectra were obtained on a Varian Cary 5000 UV-Vis-NIR spectrophotometer and photoluminescence spectra were recorded on Cary Eclipse using a quartz cuvette (Starna Cells). Ultrasound experiments were performed using a Sonics VCX 500 ultrasonic processor equipped with a 13 mm diameter removable-tip probe. The distance between the titanium tip and the bottom of the Suslick cell was 2 cm. The ultrasonic intensity was calibrated using the method outlined by Hickenboth *et al.*[3] The Suslick cells were fabricated by the Chemistry glass workshop at the University of Manchester.

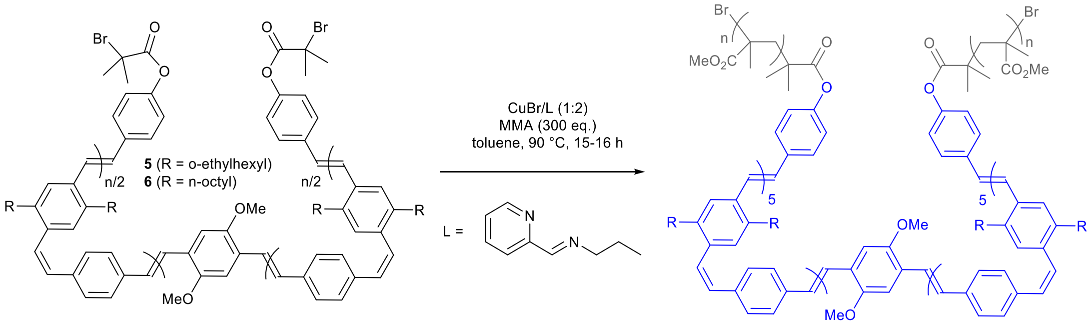
S2. ROMP of monomers 1 and 2 with catalyst 3



General experimental procedure: In an argon filled glovebox, a solution of catalyst **3** in deoxygenated anhydrous tetrachloroethane ([**M**] = 100 mM) was added into a vial containing cyclophanediene monomer **1** or **2.** The vial was sealed, wrapped in foil and mixed at room temperature for 10 minutes. The reaction was placed in a preheated oil bath at 60 °C and stirred until complete monomer conversion was observed by SEC and TLC. The reaction was cooled to room temperature, and vinyl ether *E/Z*-**4** was added. The vial was sealed, removed from the glovebox, wrapped in aluminium foil and stirred for an additional 20 hours at room temperature. The reaction was precipitated into a short methanol/Celite column, washed with methanol and the polymer extracted with chloroform. The chloroform layer was evaporated under reduced pressure to give the desired poly(*p*-phenylenevinylenes) **5**,**6** as yellow films.

(In case of alkyl monomer **2**, 3-Bromopyridine (40 mol%) was added to a solution of catalyst **3** in anhydrous dichloromethane and stirred for 20 min at room temperature. The solution was then added into a vial containing **2** followed by stirring the reaction mixture at 40 °C)

S3. Synthesis of coil-rod-coil triblock copolymers



7a (n= 403, R = 2-O-ethylhexyl)
8a (n= 479, R = n-octyl)

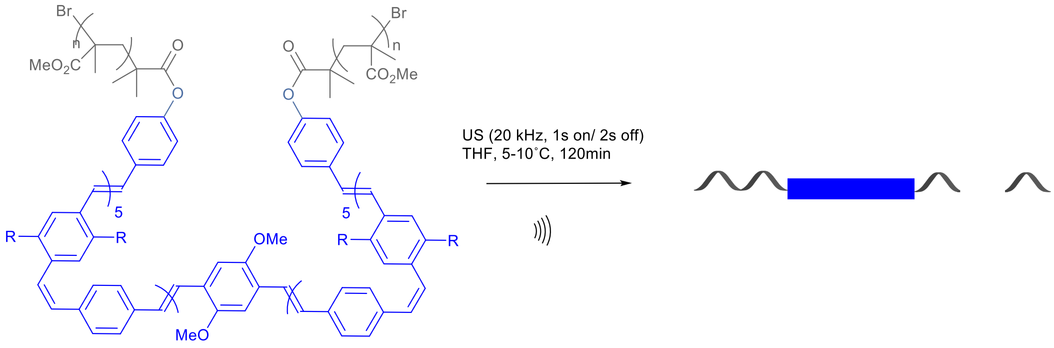
General experimental procedure for the synthesis of ABA triblock copolymers **7a:**

In an argon filled glove box, *α*-bromoester bifunctionalised poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene) (**5**, n=10) (30 mg, 5.8 µmol), degassed toluene (0.4 mL), copper(I) bromide (4.42 mg, 23.2 µmol, 4 eq), methyl methacrylate (0.37 mL, 3.48 mmol, 600 eq.) were added to a vial containing a magnetic stir bar. After 5 min, a solution of *N*-(*n*-propyl)-2-pyridylmethanimine (6.8 mg, 46.4 µmol, 8 eq.) in toluene (0.1 mL) was added into the reaction with stirring. The reaction was stirred for up to 16 h until the SEC showed the desired molecular weight. The sample was cooled to room temperature, exposed to air, precipitated into methanol and the produced solid filtered. The solid was redissolved in chloroform, reprecipitated into diethyl ether, filtered and washed with diethyl ether. After drying under vacuum PMMA-*b*-(alkoxy)PPV-*b*-PMMA triblock polymer **7a** was isolated as a yellow solid.

General experimental procedure for the synthesis of ABA triblock copolymers **8a:**

In an argon filled glove box, α-bromoester bifunctionalised PPV (**6**, n=10) (32 mg, 6 µmol), degassed toluene (0.4 mL), copper(I) bromide (4.57 mg, 24 µmol, 4 eq), methyl methacrylate (0.39 mL, 3.6 mmol, 600 eq.) were added to a glass vial containing a magnetic stir bar. After 5 min, a solution of *N*-(*n*-propyl)-2-pyridylmethanimine (7.1 mg, 48 µmol, 8 eq.) in toluene (0.1 mL) was added into the reaction with stirring. The reaction was stirred for up to 15 h until the SEC showed the desired molecular weight. The sample was cooled to room temperature, exposed to air, precipitated into methanol and the produced solid filtered. The solid was redissolved in chloroform, reprecipitated into diethyl ether, filtered and washed with diethyl ether. After drying under vacuum PMMA-*b*-(alkyl)PPV-*b*-PMMA triblock polymer **8a** was isolated as a yellow solid.

S4. General procedure for sonication



7a (n= 403, R = 2-O-ethylhexyl)
8a (n= 479, R = n-octyl)

The specified polymer (**7a** or **8a**, 30 mg) was dissolved in dry THF (15 mL) and added to a modified Suslick cell. Nitrogen was gently bubbled through the solution as it was sonicated (20 kHz, 15.6 W cm^{-2}, 1 s ON / 2 s OFF, 0 – 10 °C). After 120 minutes of sonication time, the mixture was concentrated, dried on high vacuum before being subjected to full analysis.

S5. General procedure for isomerisation

Polymer **7a** was dissolved in degassed dichloromethane (1 mg/mL) in an argon filled glovebox. The vial was sealed, removed from the glovebox and subjected to photoisomerization by irradiating with a UV lamp $\lambda = 365$ nm for 24 hours. After evaporation of the solvent the polymer **7c** was isolated as yellow solid in quantitative yield.

S6. Computational details

CoGEF simulations of polymer models were performed in Gaussian 16, Revision C.01, following Beyer's method.[4] The polymer models were optimised to their most elongated conformation with minimal bond elongations as the starting point to CoGEF simulations, to minimise computational cost. Starting from these models, the distance between pivalate terminal groups (methyl group) was constrained and incremented by 0.1 Å while minimising the energy of each step using DFT B3LYP 6-31G^{+}(d', 3p') level of theory in vacuum. The relative energy of each intermediate was determined by setting the energy of the initial state at 0 kJ/mol. F_{max} values were calculated from the slope of the energy/elongation curve (i.e. from 0.6E_{max} to E_{max}).

S7. CoGEF simulations results

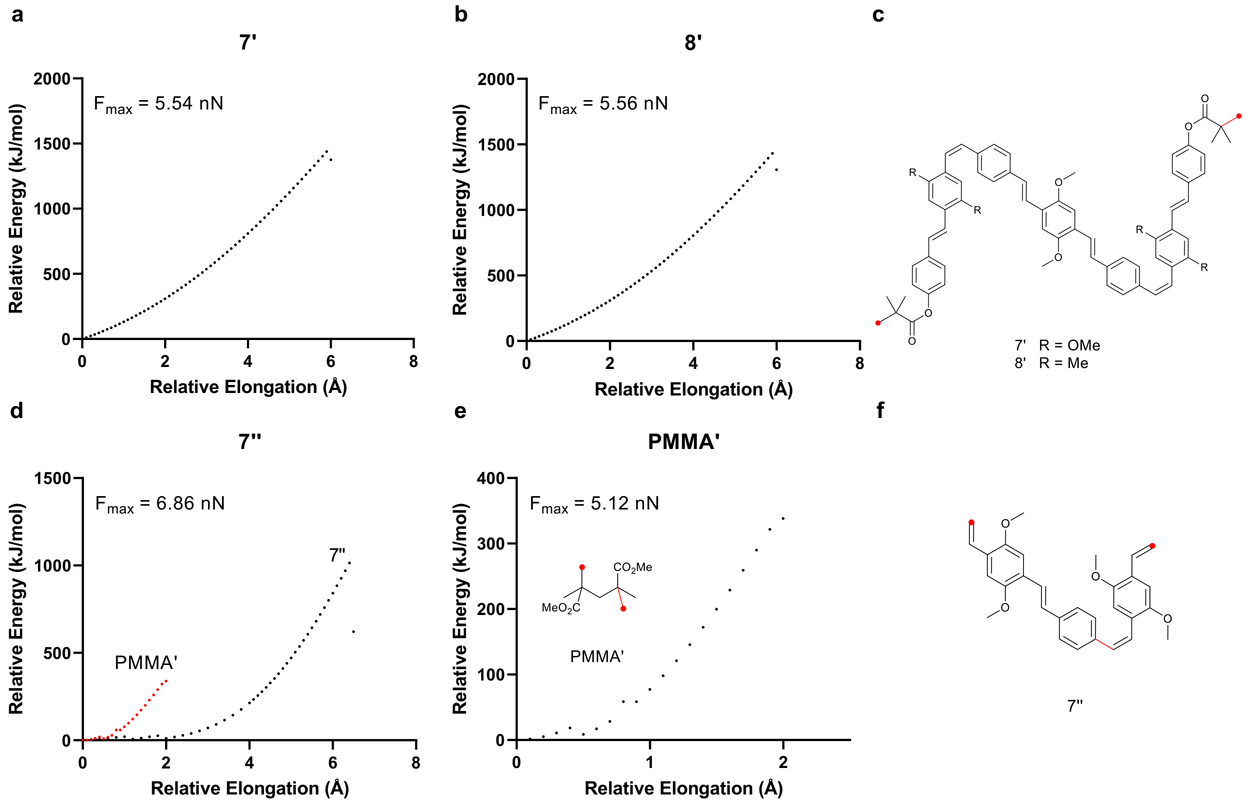


Figure S1 Relative energy of computational models of **7a** and **8a** (**7’** and **8’**, respectively) along single PPV unit (7’’) and 2 unit PMMA model (PMMA’) against the relative elongation from CoGEF simulations (a-b and d-e, respectively) and structures of 7', 8' and 7’’ (c and f, respectively). Scissile bonds were marked in red and red dots mark the constrained atoms simulating pulling force

CoGEF simulation of model of **7** were initiated from 28.0 Å separation between terminal atoms (Figure S2b) until energy visually started to rise and optimised structure was becoming more linear. Repetition of the process for model of **8** was started from elongation of 54.15 Å to save on computation time, as this distance was found to be a breakpoint to the rapid energy rise upon further structure elongation. Next, to investigate the impact of the PPV-PMMA linkage, we performed CoGEF simulations of the single PPV unit in 7a. To avoid incorporating any linkages we simply capped the units with terminal alkenes to which we have applied the geometry constraints. Upon elongation, we found that the PPV unit is likely to cleave at the ^{q}C-alkene (cis) linkage, with required force input of 6.86 nN. Also, we have computed force required to cleave a 2-unit PMMA model (PMMA’) and found it to require 5.12 nN of force to cleave the terminal methyl. It is clear that computationally predicted scission of the PPV requires significantly more force than scission of PMMA chains.

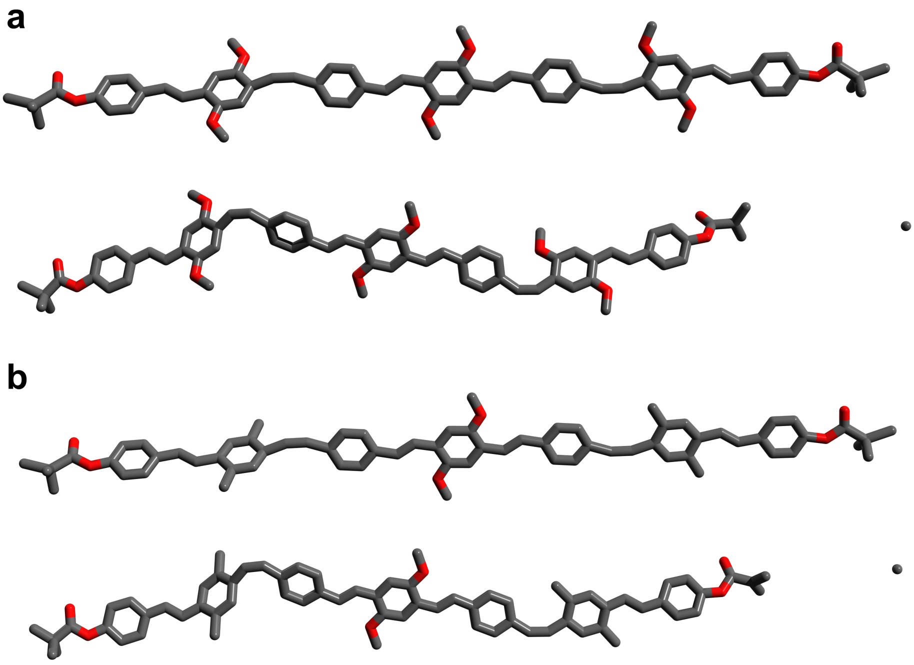
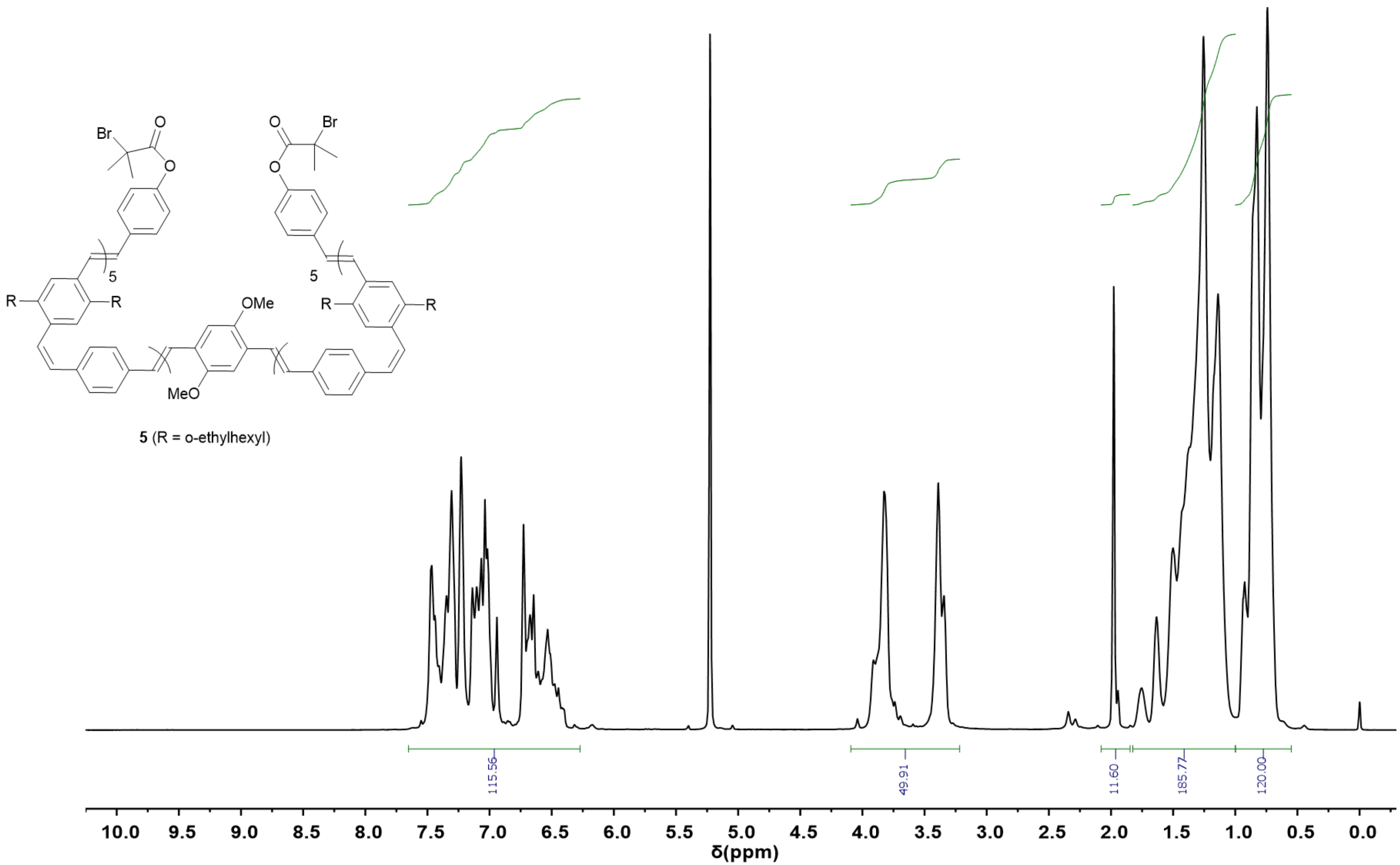


Figure S2 Structures of 7’ and 8’ (a and b, respectively) in their most elongated form and post-scission structure (top and bottom, respectively).



5 (R = o-ethylhexyl)

Figure S3 ^{1}H NMR spectrum of α-bromoester end capped PPV **5** in CD_2Cl_2.

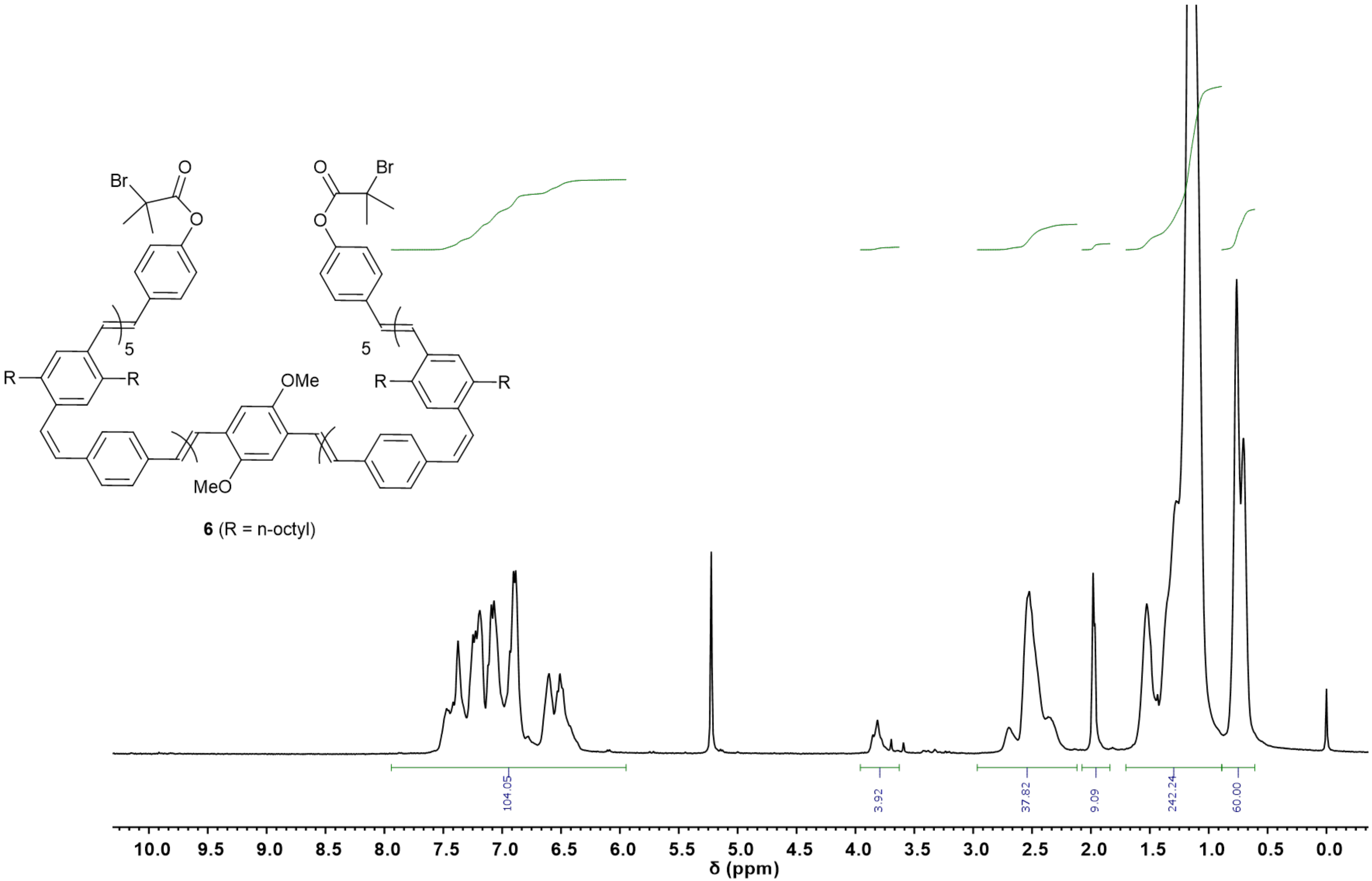
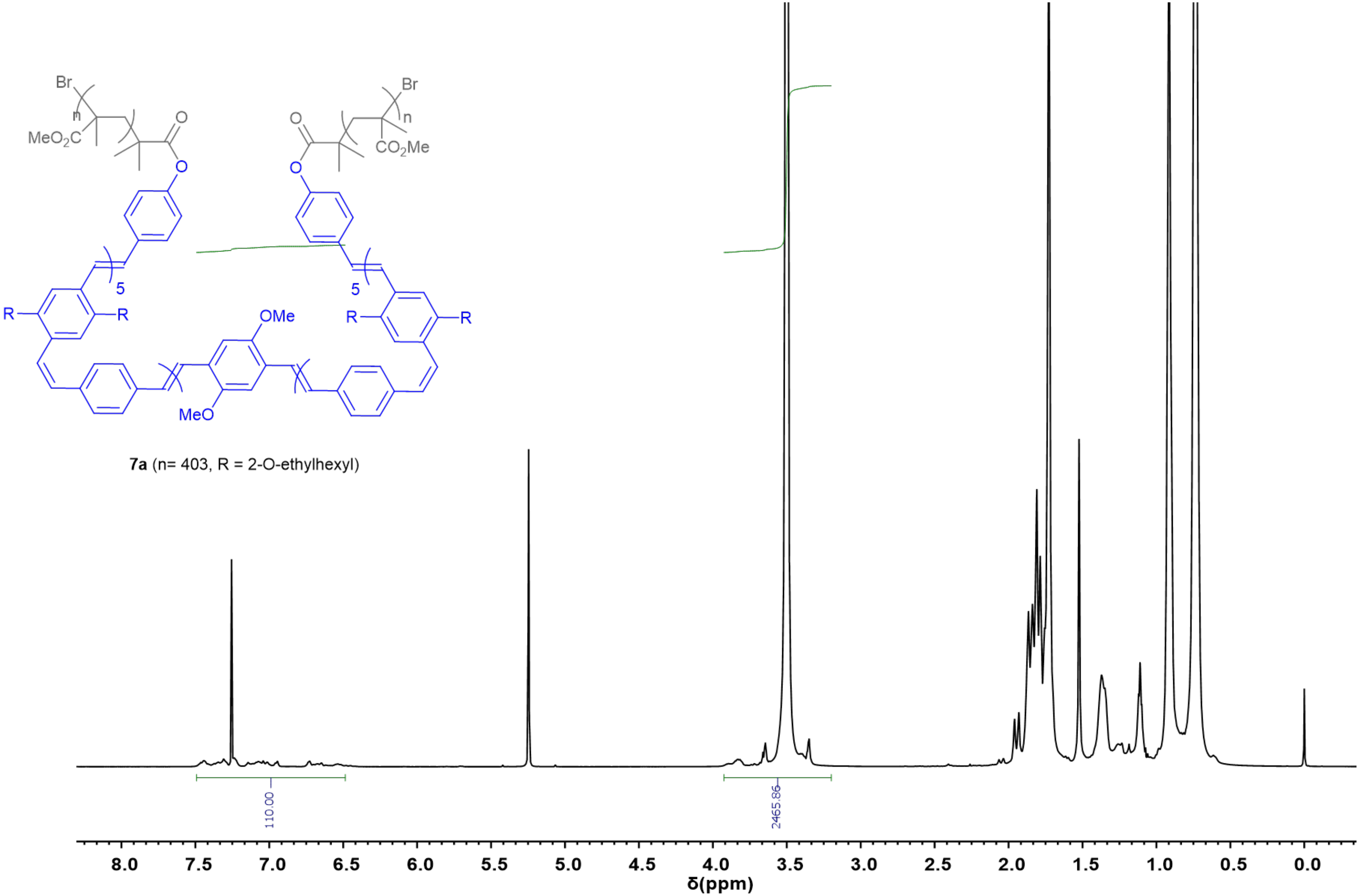


Figure S4 ^{1}H NMR spectrum of α-bromoester end capped PPV **6** in CD_2Cl_2.



7a (n= 403, R = 2-O-ethylhexyl)

Figure S5 ^{1}H NMR spectrum of BCP **7a** in CD_2Cl_2.

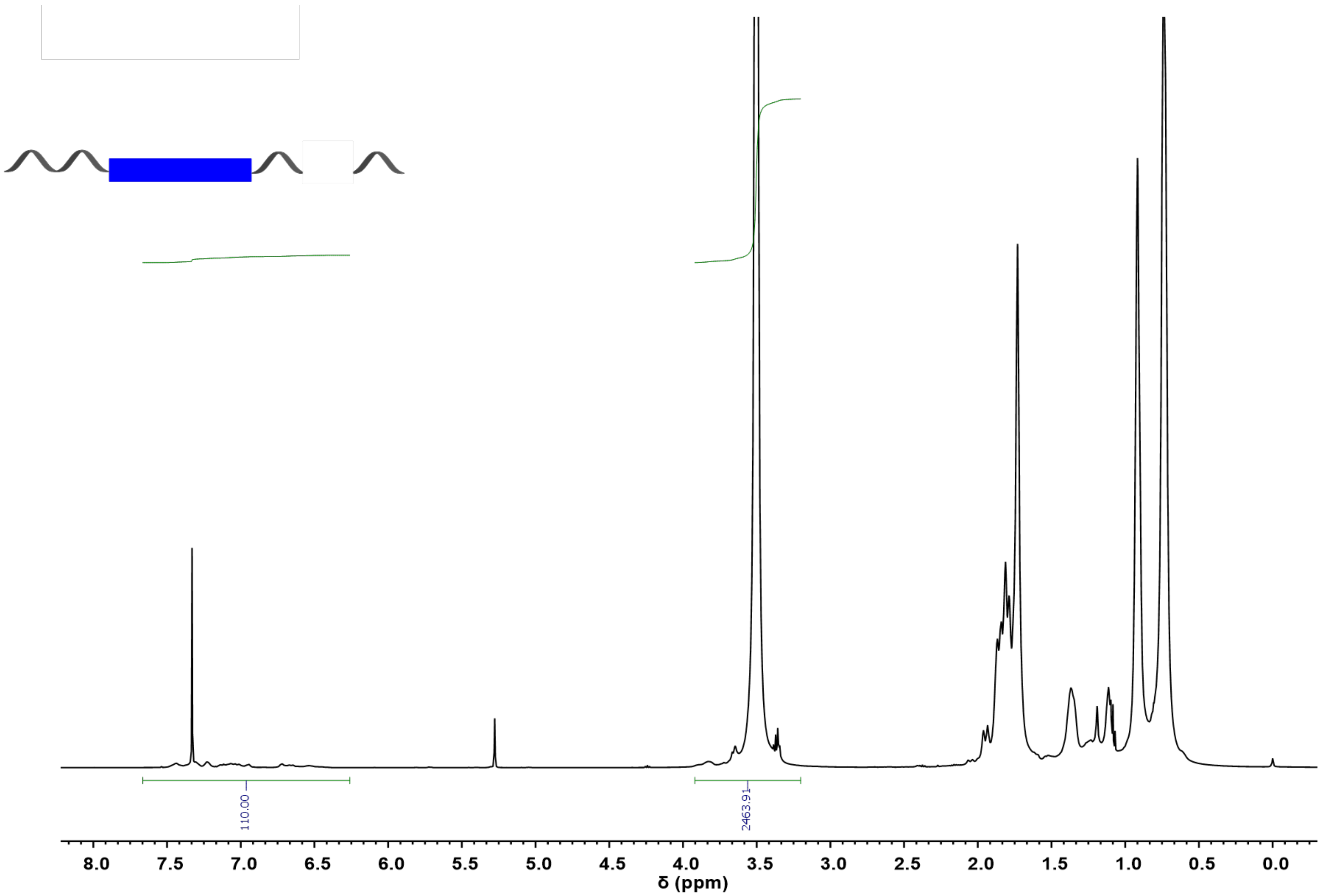


Figure S6 ^{1}H NMR spectrum of BCP **7b** in CD_2Cl_2.

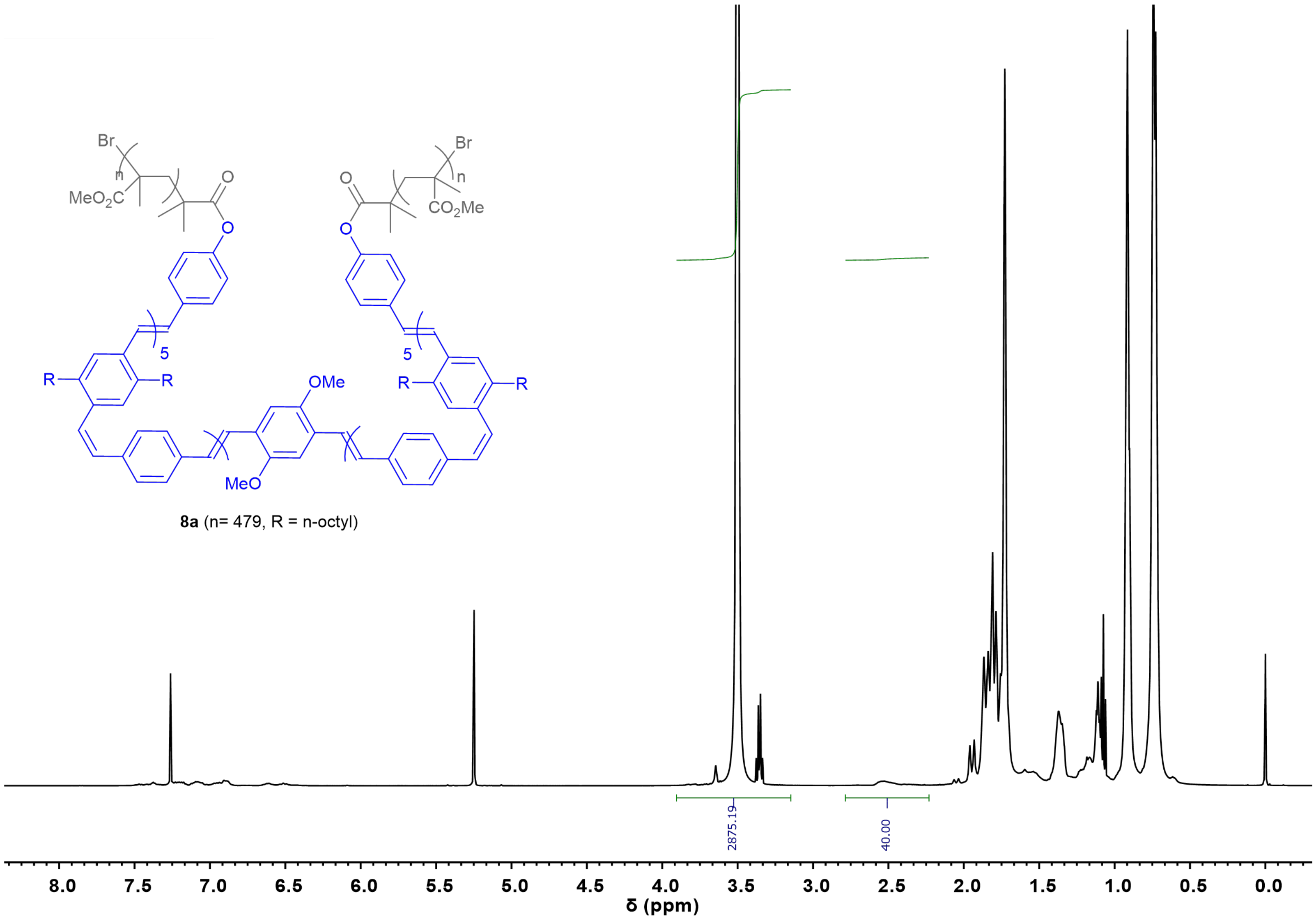


Figure S7 ^{1}H NMR spectrum of BCP **8a** in CD_2Cl_2.

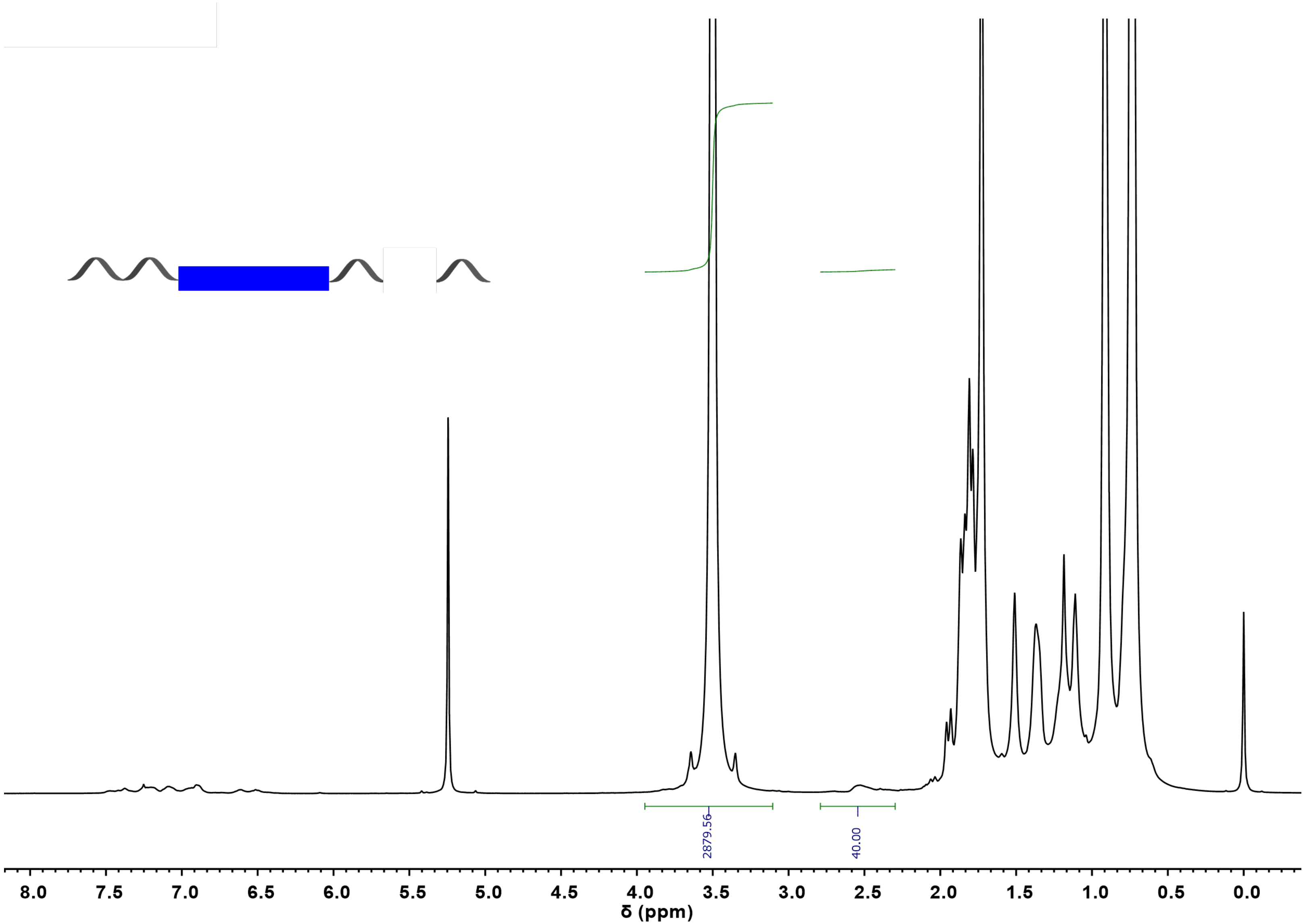
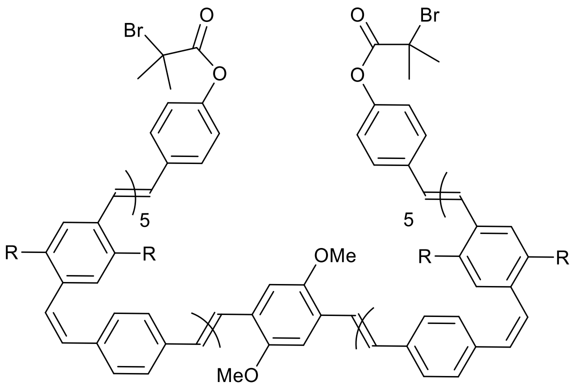
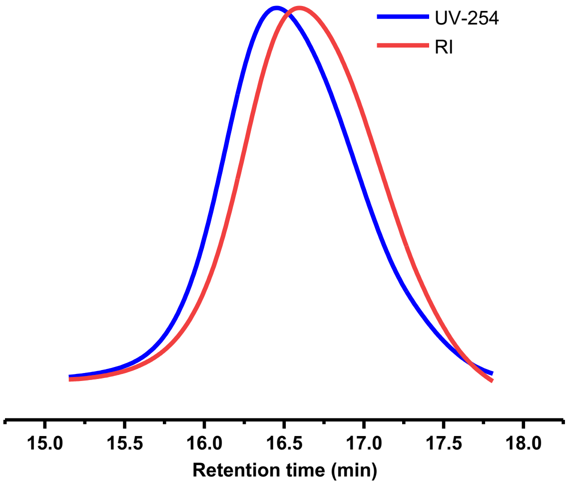
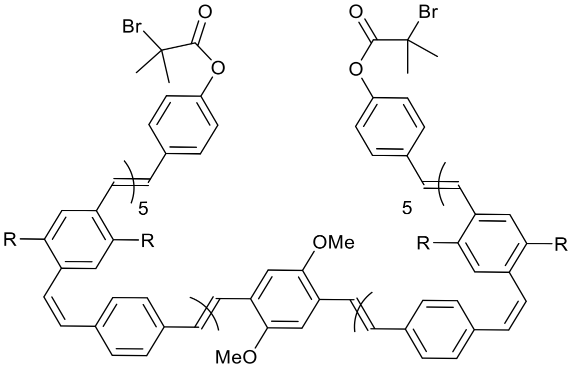
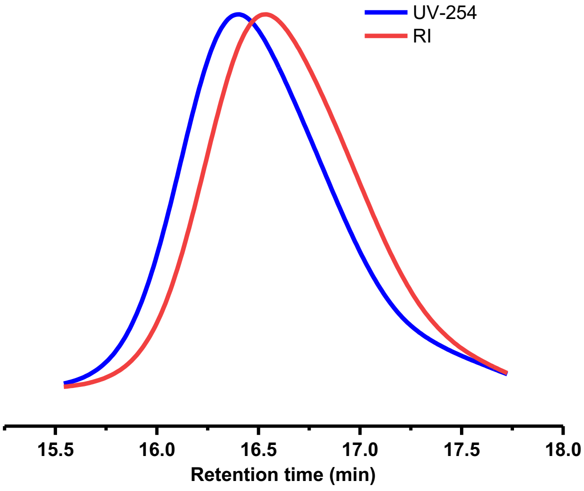
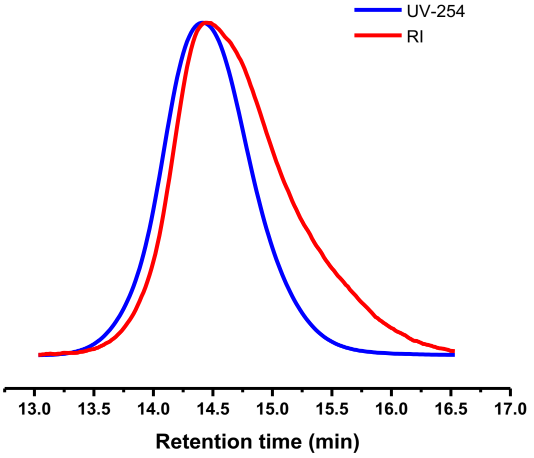
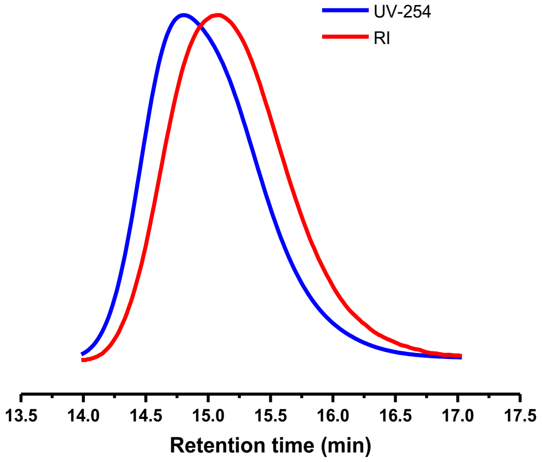
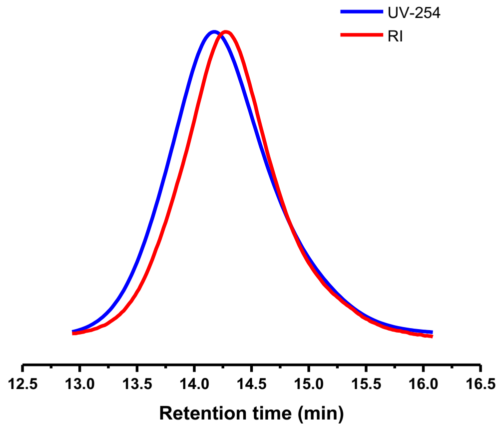
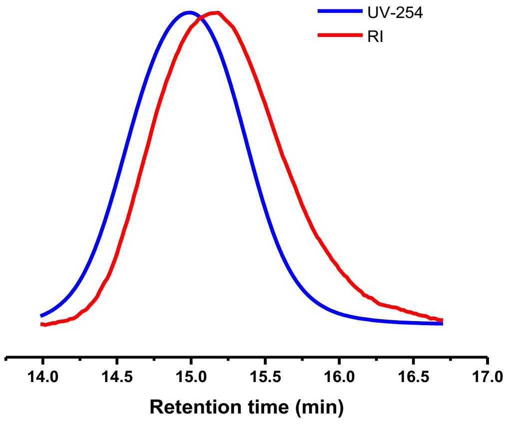


Figure S8 ^{1}H NMR spectrum of BCP **8b** in CD_2Cl_2.

S8. SEC traces

Polymer	SEC data (purified)
5  **5** (R = o-ethylhexyl)	 M_n = 5.86 kg mol^{-1} *Đ*= 1.24
6  **6** (R = n-octyl)	 M_n = 6.24 kg mol^{-1} *Đ*= 1.32

Polymer	Pre-sonication (a)	Post-sonication (b)
7	 M_n = 64310 g/mol M_p= 80970 g/mol Đ= 1.40 M_w = 89690 g/mol Structure: PMMA$_{403}$-alkoxyPPV$_{10}$- PMMA$_{403}$	 M_n = 25080 g/mol M_p= 35010 g/mol Đ = 1.42 M_w = 35570 g/mol
8	 M_n = 79300 g/mol M_p= 100580 g/mol Đ= 1.41 M_w = 111710 g/mol Structure: PMMA$_{479}$-alkylPPV$_{10}$- PMMA$_{479}$	 M_n = 25690 g/mol M_p= 30840 g/mol Đ= 1.34 M_w = 34440 g/mol

S9.Optical properties

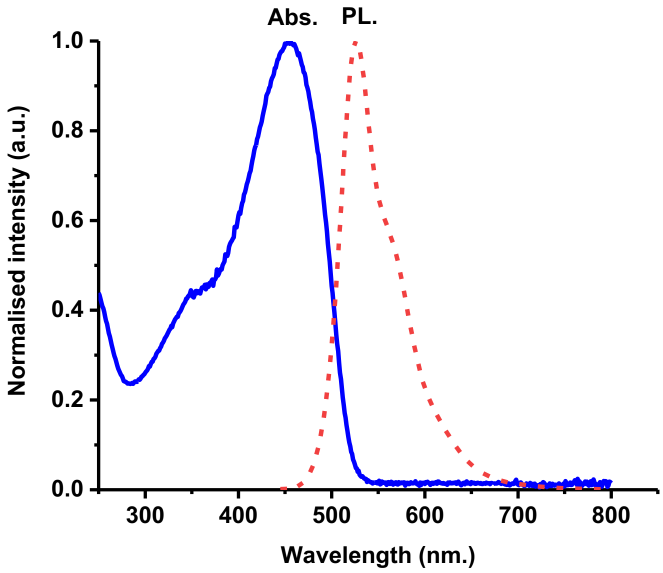


Figure S9 Absorption and emission profiles of macroinitiator **5** in $CHCl_3$ (EX=430 nm).

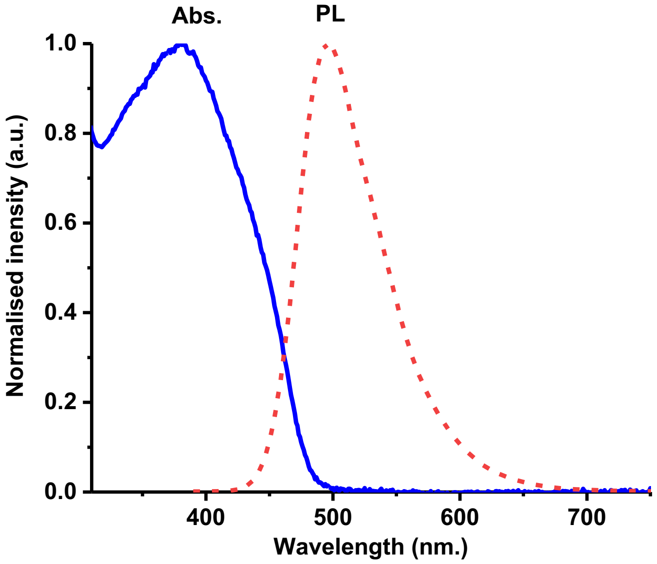


Figure S10 Absorption and emission profiles of macroinitiator **6** in $CHCl_3$ (EX=390 nm).

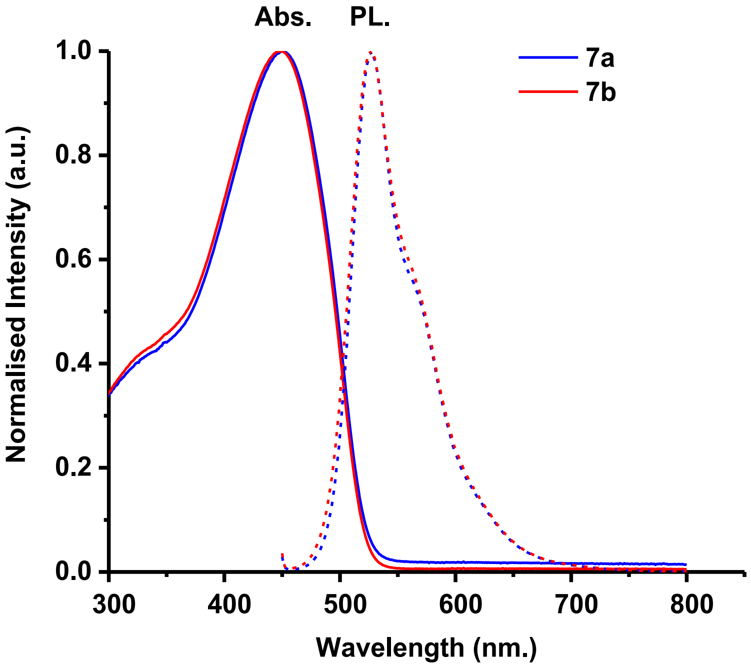


Figure S11 Absorption and emission profiles of triblock copolymers **7** in $CHCl_3$ (EX=440 nm).

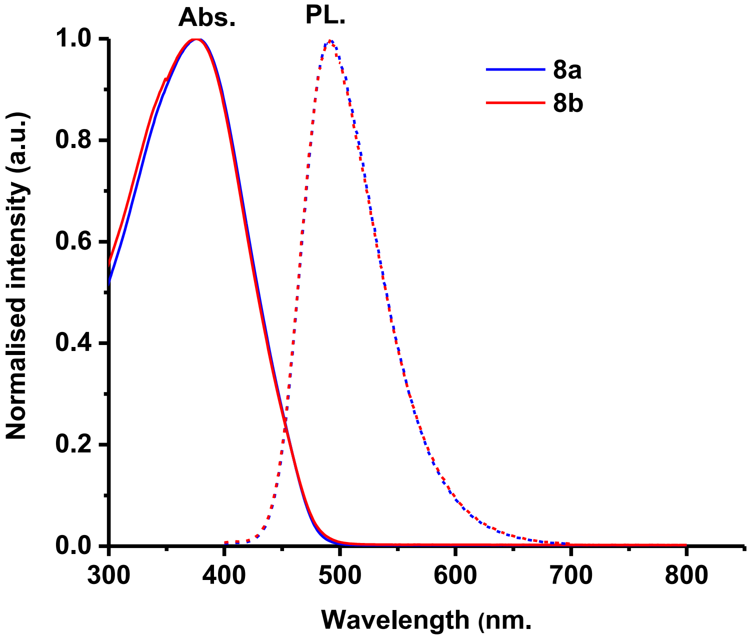


Figure S12 Absorption and emission profiles of triblock copolymers **8** in $CHCl_3$ (EX=370 nm).

S10. References

1 B. J. Lidster, J. M. Behrendt and M. L. Turner, *Chem. Commun.*, 2014, **50**, 11867–11870.

2 B. J. Lidster, D. R. Kumar, A. M. Spring, C.-Y. Yu and M. L. Turner, *Polym. Chem.*, 2016, **7**, 5544–5551.

3 C. R. Hickenboth, J. S. Moore, S. R. White, N. R. Sottos, J. Baudry and S. R. Wilson, *Nature*, 2007, **446**, 423–427.

4 M. K. Beyer, *J. Chem. Phys.*, 2000, **112**, 7307–7312.