

## Supporting Information

# Flash-Synthesis of Low Dispersity PPV via Anionic Polymerization in Continuous Flow Reactors and Block Copolymer Synthesis

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### Analysis

Proton magnetic resonance (<sup>1</sup>H NMR) and Carbon magnetic resonance (<sup>13</sup>C NMR) spectra were recorded in deuterated chloroform (CDCl<sub>3</sub>) on a Jeol 400 Mhz spectrometer. The chemical shifts (δ) are recorded in ppm relative to tetramethylsilane (δ = 0 ppm), referenced to the chemical shift of the residual solvent (CDCl<sub>3</sub>) resonances (<sup>1</sup>H). FT-IR spectra were collected with a Bruker Tensor 27 FT-IR spectrophotometer (nominal resolution 4 cm<sup>-1</sup>). Size exclusion chromatography (SEC) was used for the analysis of the molecular weight distributions of the polymer samples. The system is a Tosoh EcoSEC, comprising an autosampler, a PSS guard column SDV (50 x 7.5 mm), followed by three PSS SDV analytical linear XL columns (5 μm, 300 x 7.5 mm) and a differential refractive index detector (Tosoh EcoSEC RI) using THF as the eluent at 40°C with a flow rate of 1 mL·min<sup>-1</sup>. The SEC system was calibrated using linear narrow polystyrene standards ranging from 474 to 7.5 x 10<sup>6</sup> g·mol<sup>-1</sup> (PS (K = 14.1 x 10<sup>-5</sup> dL·g<sup>-1</sup> and α = 0.70)). Polymer concentrations were in the range of 3-5 mg·mL<sup>-1</sup>. Mark Houwink parameters for plain precursor (α = 0.67605 and k = 0.000142 mL·g<sup>-1</sup>) and conjugated (MDMO)-PPV (α = 0.809 and

$k = 0.00002 \text{ mL}\cdot\text{g}^{-1}$ ) were used. UV-Vis spectra were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer (scan rate  $600 \text{ nm}\cdot\text{min}^{-1}$ , continuous run from 200 to 800 nm).

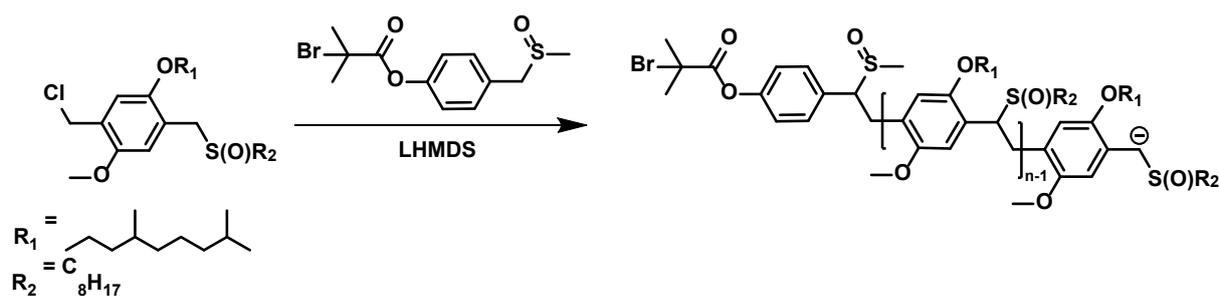
### Synthesis of the MDMO sulfinyl premonomer: 1-(Chloromethyl)-5-((3,7-dimethyloctyl)oxy)-2-methoxy-4-((octylsulfinyl)methyl)benzene (MDMO)

The synthesis of the MDMO premonomer was performed as described in literature procedures.<sup>i</sup>

### Synthesis of the anionic initiator: 4-((methylsulfinyl)methyl)phenyl-2-bromo-2-methylpropanoate

The synthesis of the initiator was performed as described in literature procedures.<sup>ii,iii</sup>

### General method for the synthesis of the MDMO-PPV precursor polymer (Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)]-1,4-phenylenevinylene) in a tubular flow reactor



Scheme 1: Synthesis of the MDMO-PPV precursor polymer via the anionic sulfinyl precursor route

The MDMO premonomer (585 mg, 1.2 mmol, 1 equiv) and the initiator (76.6 mg, 0.24 mmol, 0.2 equiv) were added into separate vials and both were transferred into the glovebox where the compounds were dissolved in THF (20 mL and 18.44 mL respectively). The base LHMDS (1M in THF) (261 mg, 1.56 mL, 1.56 mmol, 1.3 equiv) was added to the vial containing the initiator. The monomer-initiator-base ratio of 1/0.2/1.3 was chosen because this initiator concentration gives generally the lowest dispersity and the LHMDS base needs to activate both the MDMO premonomer and the initiator. Two 25 mL gastight syringes were filled with the solutions which were then connected to the Y-piece that was capped with a stop at the end. Everything was transferred out of the glovebox and the Y-piece was connected to the reactor together with the quenching line. The reagent solutions were pumped into

the reactor with the syringe pumps and the polymer was formed at room temperature. The precursor polymer was collected as a yellow viscous oil and was poured into H<sub>2</sub>O (40 mL) before extraction with CH<sub>2</sub>Cl<sub>2</sub> (3 x 50 mL). The solvent was evaporated and the precursor polymer was precipitated in cold MeOH (40 mL). Filtration on a Teflon<sup>®</sup> filter resulted in the purified precursor polymer as a bright yellow sticky oil.

### **General method for the synthesis of the block copolymer**

The synthesis of the block copolymer was performed as described in literature procedures.<sup>Error! Bookmark not defined.</sup>

### **General method for the elimination of the block copolymer**

The elimination of the block copolymer was performed as described in literature procedures.<sup>Error! Bookmark not defined.</sup>

### **<sup>1</sup>H NMR of various PPV precursor polymers**

The following <sup>1</sup>H NMR data confirms the polymer structure and the presence of the Br-end group. The 2 CH<sub>3</sub> groups adjacent to the terminal bromine appear at 2.06 and 2.08 ppm.

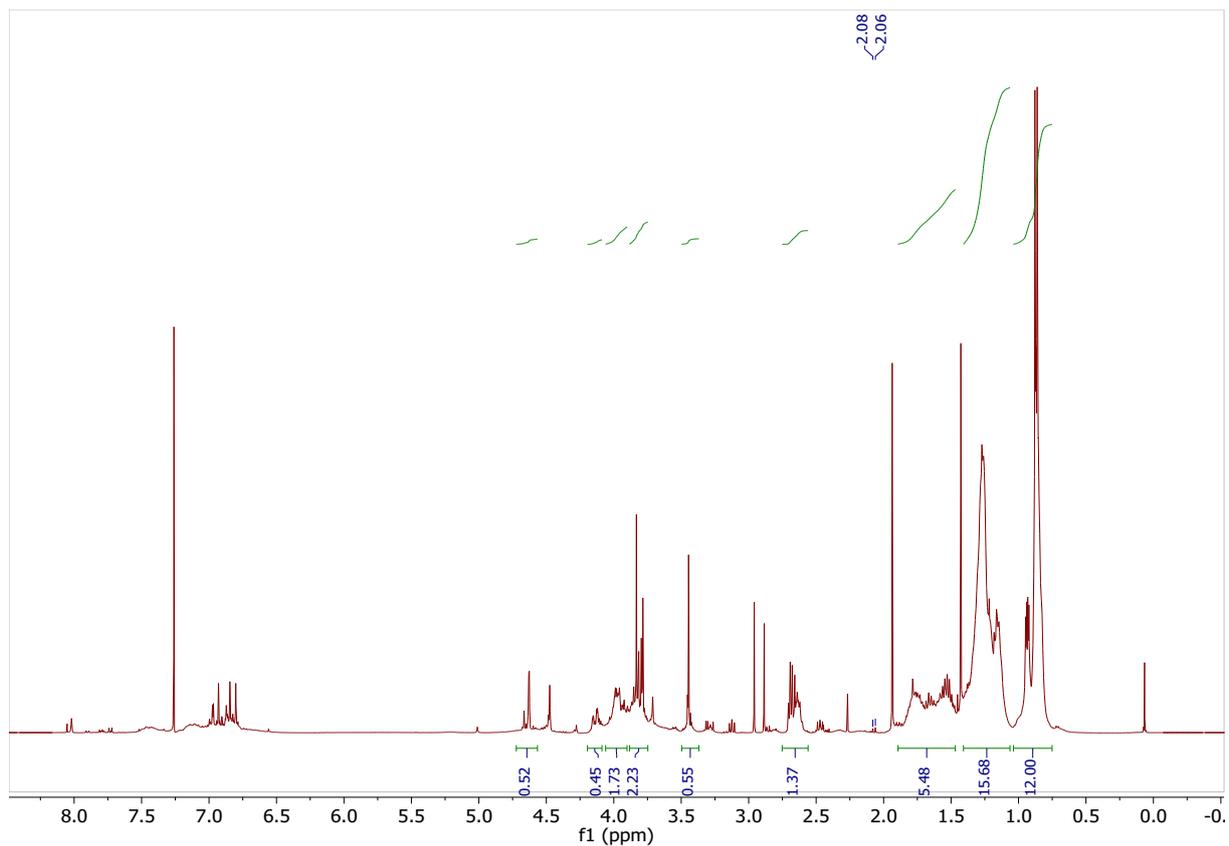


Figure 1:  $^1\text{H}$  NMR of the PPV precursor polymer with a flow reactor of 0.5 mL and a residence time of 10 seconds

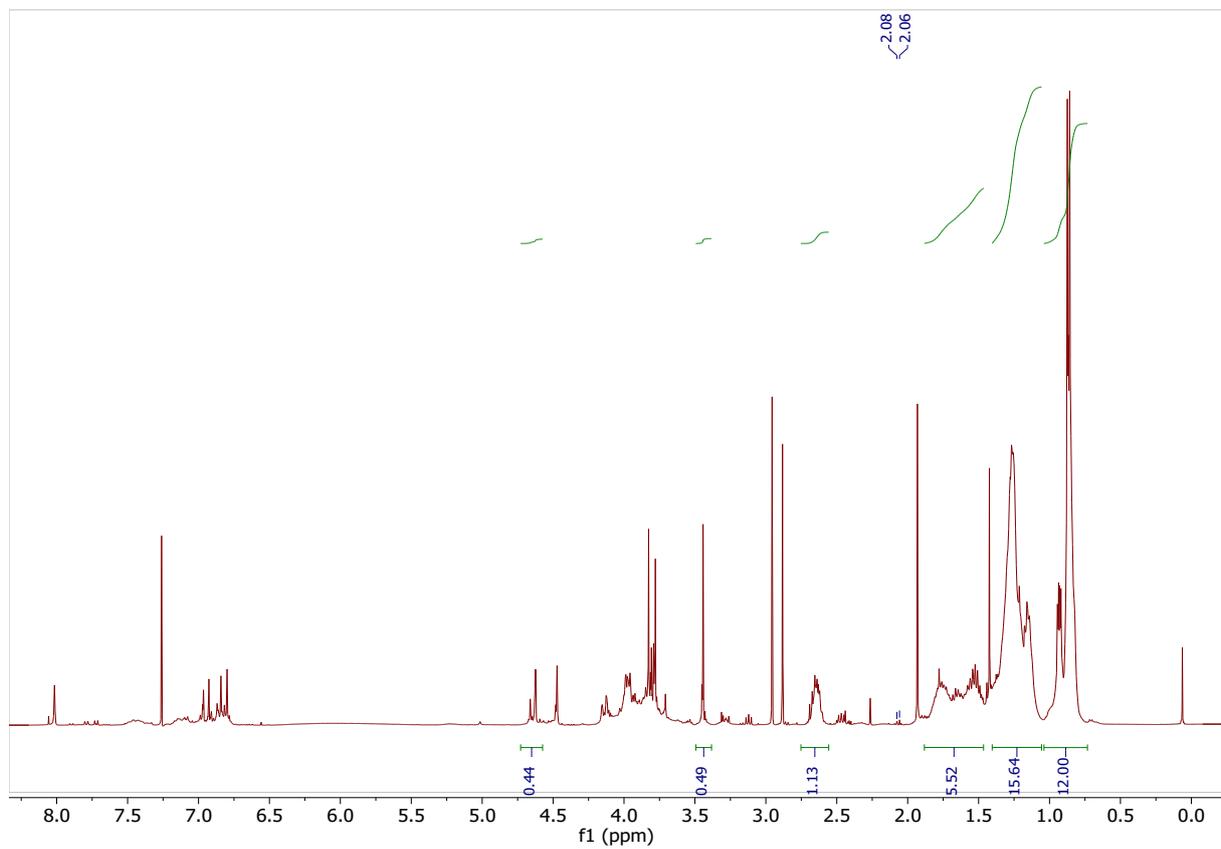


Figure 2:  $^1\text{H}$  NMR of the PPV precursor polymer with a flow reactor of 0.5 mL and a residence time of 1 second

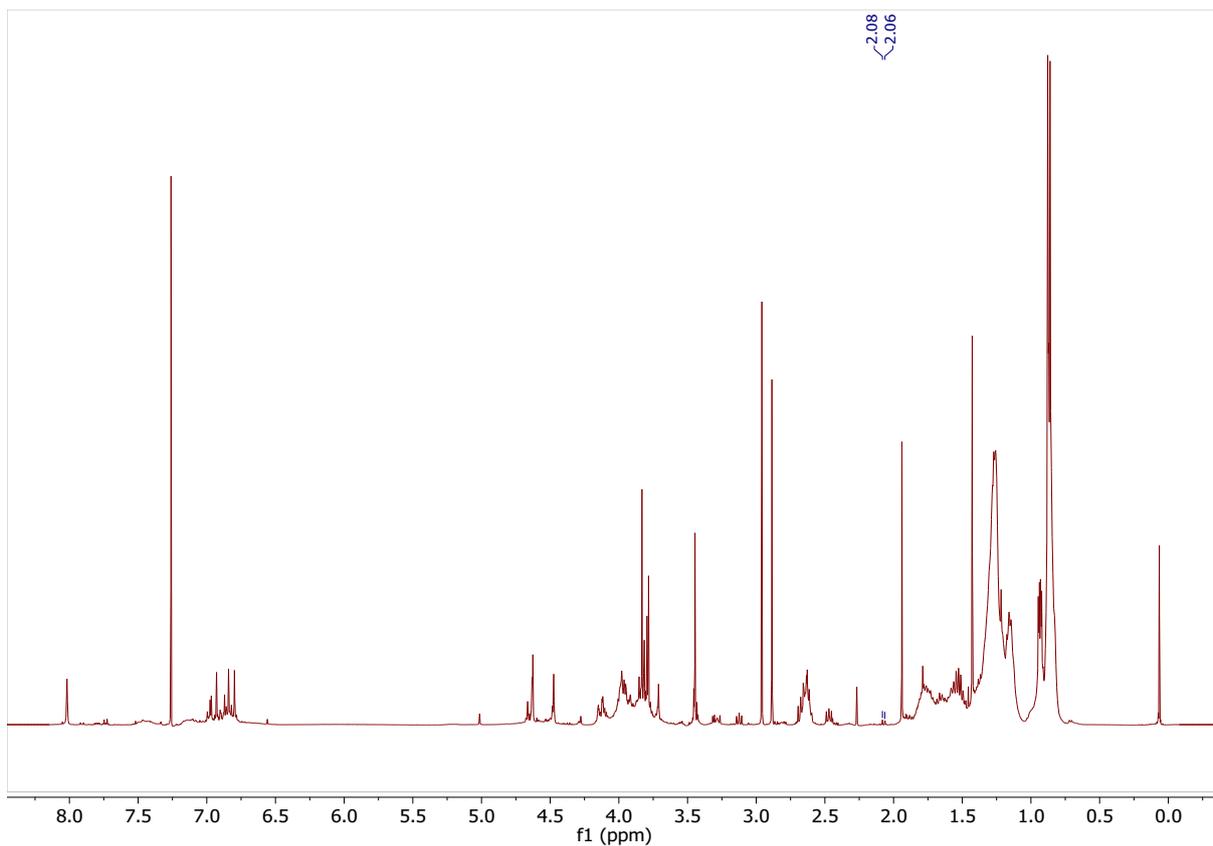


Figure 3: <sup>1</sup>H NMR of the PPV precursor polymer with a flow reactor of 0.13 mL and a residence time of 1 second

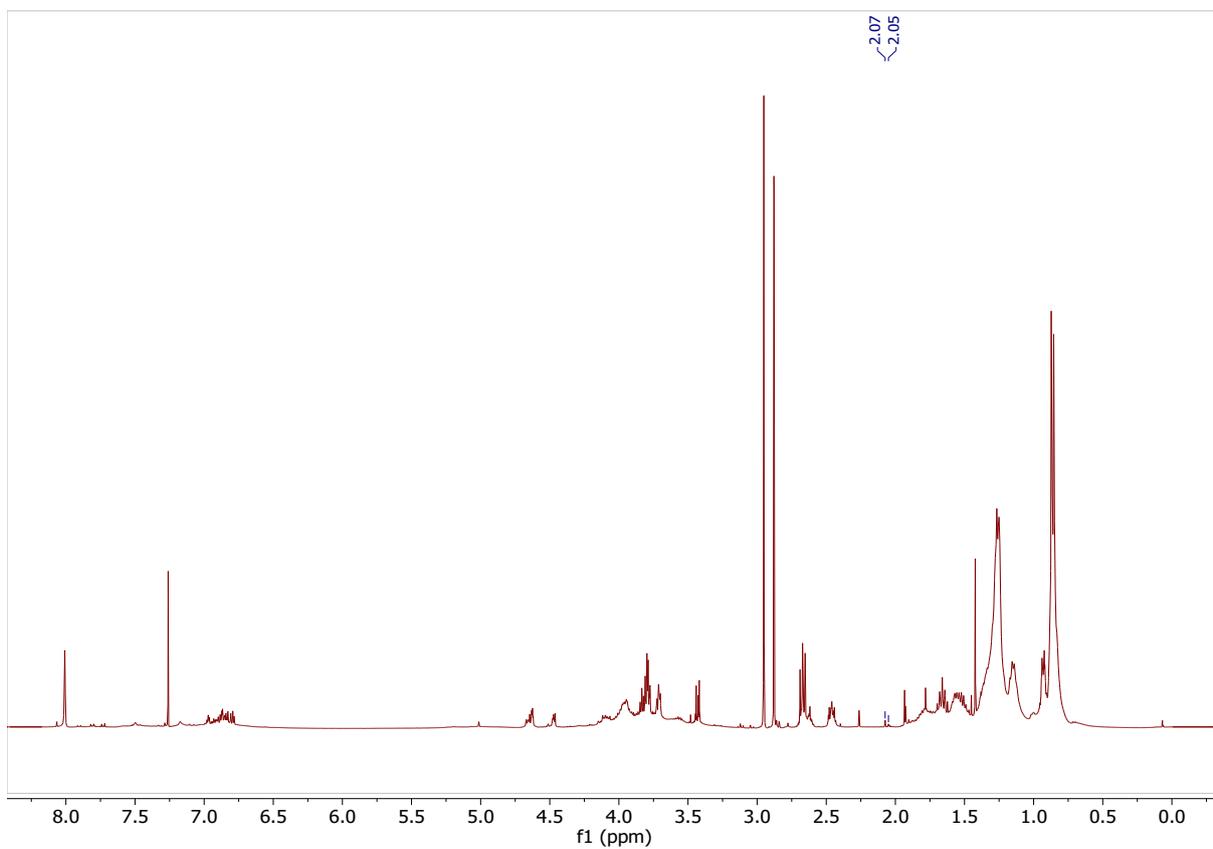


Figure 4: <sup>1</sup>H NMR of the PPV precursor polymer with a flow reactor of 0.13 mL and a residence time of 0.25 seconds

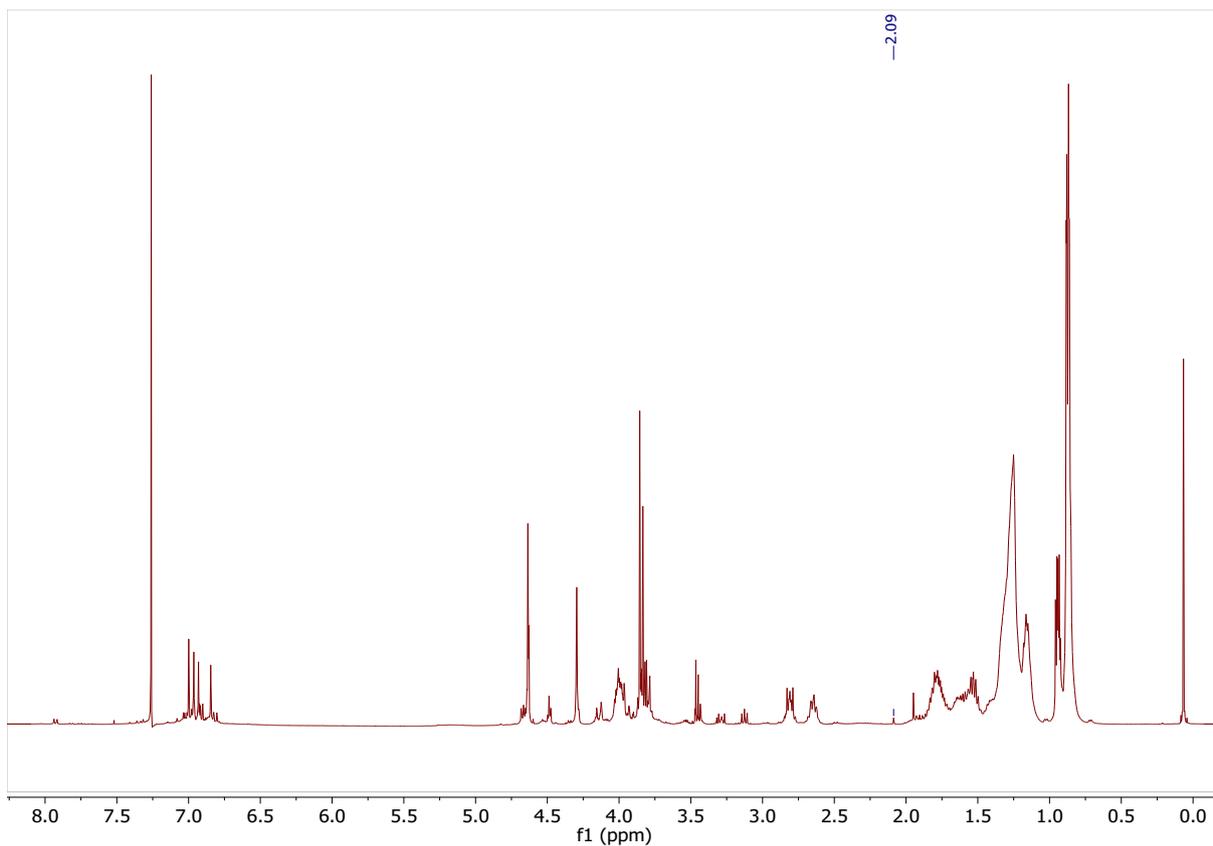


Figure 5: <sup>1</sup>H NMR of the PPV precursor polymer without a flow reactor and a residence time of 0.05 seconds

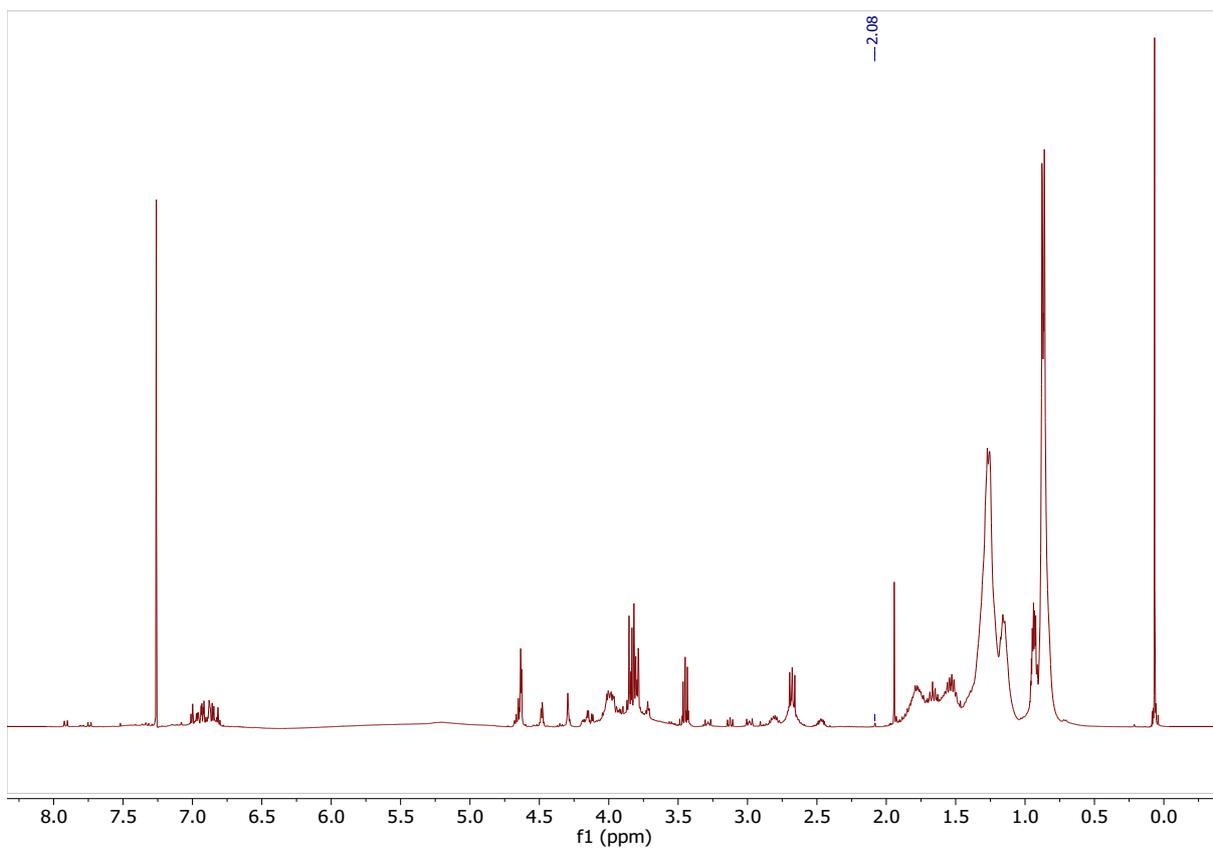
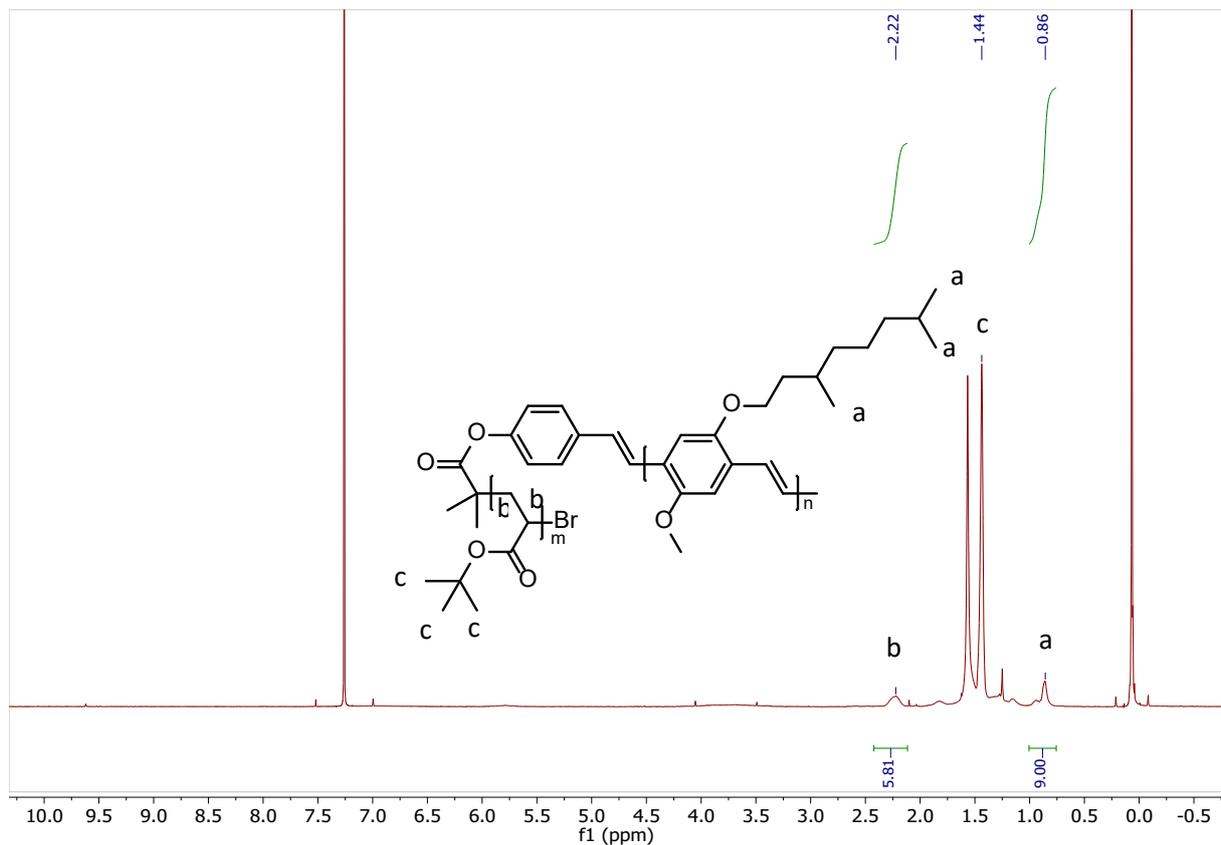


Figure 6: <sup>1</sup>H NMR of the PPV precursor polymer without a flow reactor and a residence time of 0.0032 seconds

## Calculation of the molecular weight of the block copolymers via $^1\text{NMR}$



The signal at 0.86 ppm corresponds to the 3  $\text{CH}_3$  groups of MDMO PPV (indicated a) and the integration is therefore set at 9 rel. The signal at 2.22 ppm corresponds to 3 protons that belong to the *t*BuA polymer (indicated b). In this example this peak integrates for 5.81 rel, to calculate the degree of polymerization for the *t*BuA block the following calculation is done:

$$\frac{5.81 \text{ rel}}{3 \text{ rel}} = 1.9$$

This means there are 1.9 times more *t*BuA block in the block copolymer than PPV blocks.

The molecular weight of the PPV block is determined using SEC and is  $16700 \text{ g} \cdot \text{mol}^{-1}$  and the molecular weight of one block is  $288 \text{ g} \cdot \text{mol}^{-1}$ , the DP is:

$$\frac{16700 \text{ g} \cdot \text{mol}^{-1}}{288 \text{ g} \cdot \text{mol}^{-1}} = 58 \text{ PPV units}$$

The DP for the *t*BuA block is therefore:

$$1.9 \cdot 58 \text{ units} = 110 \text{ tBuA units}$$

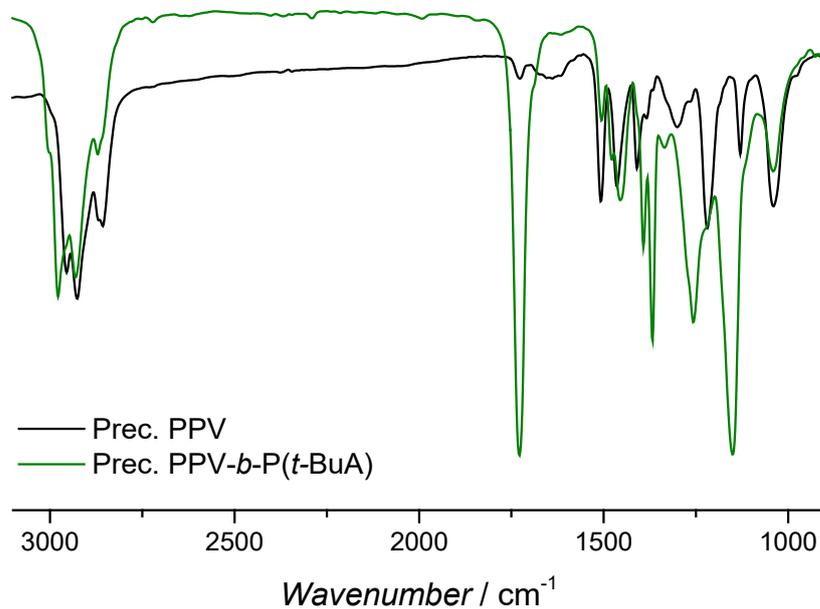
The molecular weight of the tBuA block is:

$$110 \text{ tBuA units} \cdot 128 \text{ g} \cdot \text{mol}^{-1} = 14100 \text{ g} \cdot \text{mol}^{-1}$$

This means the total molecular weight of the block copolymer is:

$$16700 \text{ g} \cdot \text{mol}^{-1} + 14100 \text{ g} \cdot \text{mol}^{-1} = 30800 \text{ g} \cdot \text{mol}^{-1}$$

#### FT-IR of the PPV precursor homopolymer and the precursor PPV-*b*-P(*t*-BuA) block copolymer



#### Micelle synthesis in a tubular flow reactor

The micelle formation in a tubular flow reactor was performed as described in literature procedures.<sup>iv</sup>

## DLS of micelles obtained in the flow self-assembly procedure

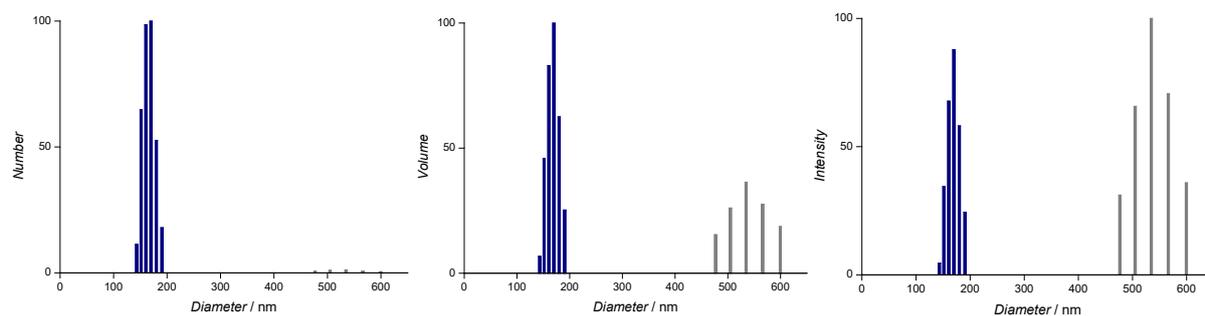


Figure 7: DLS graphs showing number, volume and intensity average diameter of the micelles from PPV-b-PAA

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<sup>i</sup> F. Louwet, D. Vanderzande, J. Gelan, J. Mullens, *Macromolecules* **1995**, *28*, 1330-1331.

<sup>ii</sup> I. Cosemans, J. Vandenberghe, L. Lutsen, D. Vanderzande, T. Junkers, *Polym. Chem.* **2013**, *4*, 3471-3479.

<sup>iii</sup> H. Becker, H. Spreitzer, K. Ibrom, W. Kreuder, *Macromolecules* **1999**, *32*, 4925-4932.

<sup>iv</sup> A. Buckinx, K. Verstraete, E. Baeten, R. F. Tabor, A. Sokolova, N. Zaquen, T. Junkers, *Angewandte* **2019**, *58*, 13799-13802.