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## SUPPORTING INFORMATION

### Anionic PPV Polymerization from the Sulfinyl Precursor Route: Block Copolymer Formation from Sequential addition of Monomers

*Inge Cosemans,<sup>a</sup> Joke Vandenbergh,<sup>a</sup> Vincent Voet,<sup>b</sup> Katja Loos,<sup>b</sup> Laurence Lutsen,<sup>c</sup> Dirk Vanderzande<sup>a,c</sup> and Thomas Junkers\*<sup>a</sup>*

#### **Analysis**

UV-Vis spectra were recorded on a Varian Cary 500 UV-Vis-NIR spectrophotometer (scan rate 600 nm/min, continuous run from 200 to 800 nm). Fluorescence measurements were performed using a 'Fluorolog® Tau-3 Lifetime System' spectrofluorometer from Horiba Group, USA. The entire system was controlled by DataMax software. The excitation wavelength was kept at 466 and 495 nm and the emission was scanned between respectively 490 or 520 and 800 nm. The sample was placed at an angle of 22.5°, resulting in the highest fluorescence signal with a minimum of scattering and reflection coming from the glass. The slits of both monochromators were adjusted to 5 nm. Analysis of the MWD of the polymer with UV detection at 466nm was performed using a Spectra Series P100 (Spectra Physics) pump equipped with two mixed-B columns (10 µm, 2 cm x 30 cm, Polymer Laboratories) and a Agilent 1100 DAD UV detector at 60°C. Chlorobenzene (CB) was used as the eluent at a flow rate of 1.0 mL/min. Molecular weights were determined relative to polystyrene standards. Differential scanning calorimetry (DSC) measurements were performed on a TA instruments Q200 DSC, purged with nitrogen. About 5 mg samples were sealed in aluminum crucibles (Tzero, 40 µL). The scan rate was 20 °C·min<sup>-1</sup> for temperatures ranging from -90 °C

– 120 °C. Three heating-cooling cycles were run to check the reproducibility. Thermo gravimetric analysis (TGA) was performed on a TA instruments HiRes TGA 2950 Thermo gravimetric analyzer with a heating rate of 10 °C·min<sup>-1</sup>.

### Characterization for BEH-PPV-*b*-P(*t*-BuA) **P2**

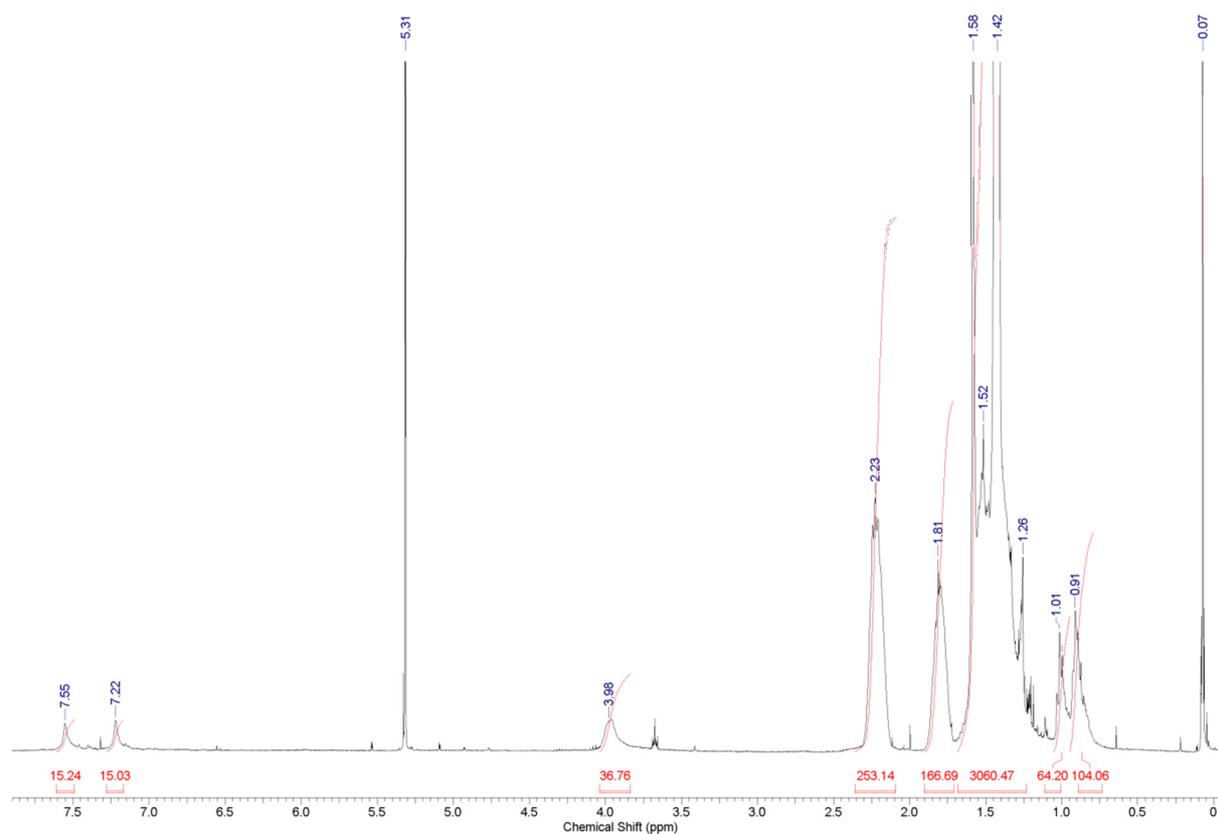


Figure S1: <sup>1</sup>H NMR spectrum of block copolymer **P2** in CD<sub>2</sub>Cl<sub>2</sub>

In the UV-Vis spectrum (Figure S2), a blue-shift in  $\lambda_{\max}$  is observed if the blockcopolymer **P2** (466nm) is compared to the pure PPV **P1** (495nm). So, by introducing the *tert*-butyl block, the average conjugation length becomes shorter than for the pure PPV, meaning that the acrylate is slightly disrupting the optimal conjugation of the PPV block. The same result is found in the fluorescence spectrum, where also a blue-shifted maximal wavelength is found for the blockcopolymer compared to the pure BEH-PPV.

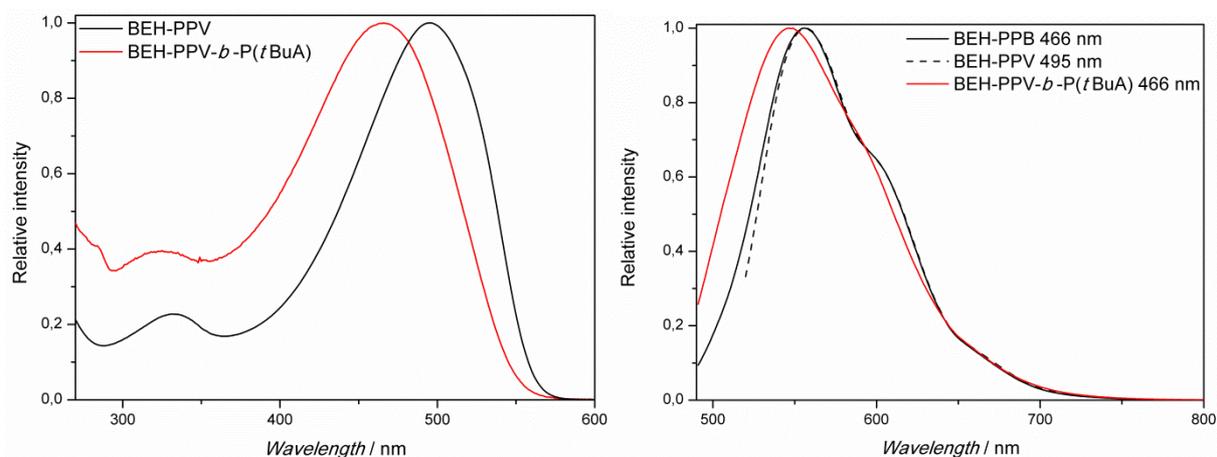


Figure S2: UV-Vis and fluorescence spectra measured in  $\text{CHCl}_3$  solution for BEH-PPV **P1** and BEH-PPV-*b*-P(*t*-BuA) **P2**

To confirm the presence of a block copolymer also a GPC trace was measured with UV detection at 466 nm (CB as eluent), the maximum absorption wavelength for **P2** (see Figure S2). From these data (see also Table S1), it can clearly be concluded that the acrylate block is connected to the PPV block.

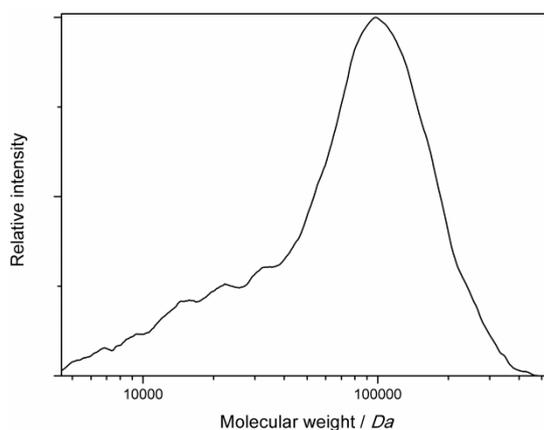


Figure S3: GPC profile of **P2** for UV detection at 466nm

Table S1: Molecular weight and PDI for **P2** (UV detection at 466nm)

<b>Conjugated polymer</b>		
	$M_n^{\text{app}}$ (g·mol <sup>-1</sup> )	PDI
<b>After purification, high MW fraction</b>	43900	2.1

In the DSC profile (Figure S4), a glass transition ( $T_g$ ) is visible at 34.7 °C. This glass transition can be addressed to the acrylate block. For the PPV block, no  $T_g$  could be observed in this measurement.

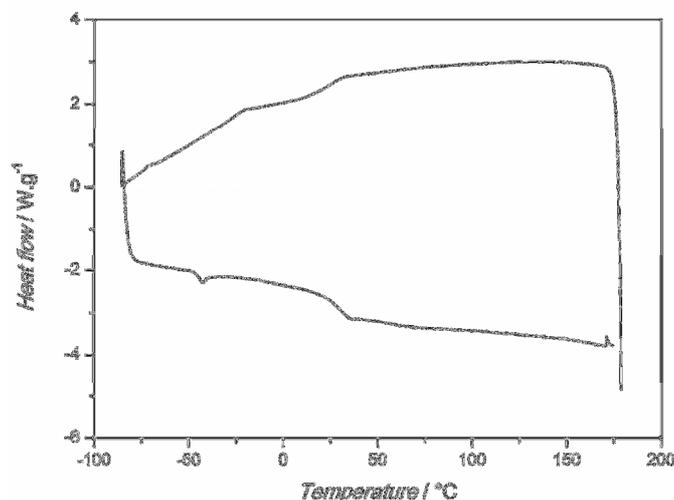


Figure S4: DSC profile for PPV-*b*-P(*t*-BuA) **P2**

To study the thermal stability of the polymers, the weight loss is recorded as a function of temperature in thermo gravimetric analysis. From the TGA profile (Figure S5), it can be observed that vaporization starts around 210  $^{\circ}C$ . The second major weight loss with a maximum around 432  $^{\circ}C$  accounts for the degradation of the conjugated system.

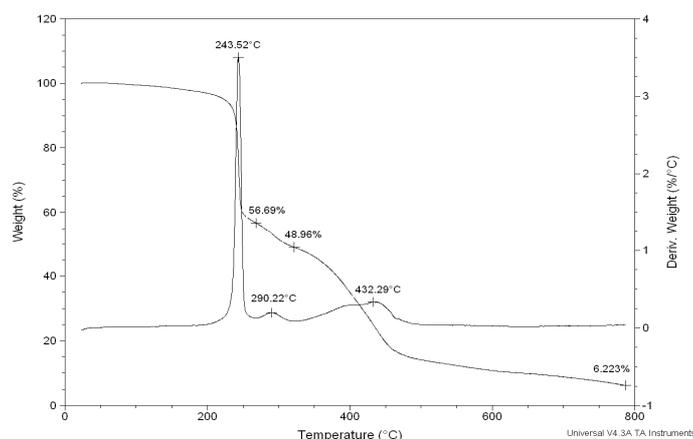


Figure S5: TGA profile for PPV-*b*-P(*t*-BuA) **P2**