

SUPPORTING INFORMATION

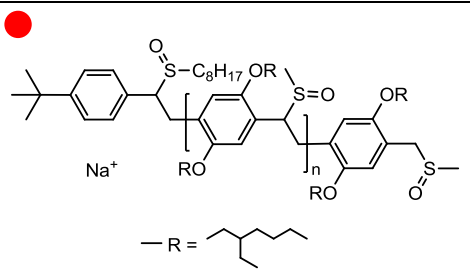
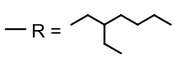
Synthesis of well-defined PPV containing block polymers with precise endgroup control from a dual-initiator strategy

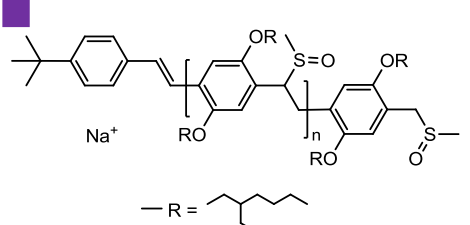
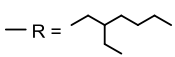
Inge Cosemans,^a Joke Vandenberg,^a Laurence Lutsen,^b Dirk Vanderzande^{a,b} and Tanja Junkers*^a

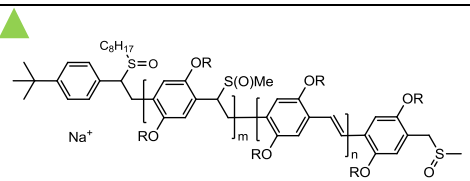
ESI-MS values compared to calculated values and polymer structures for P1', P2', P1 and P2

Precursor polymer with *tert*-butyl initiator (P1')

Table S1: Comparison between measured and calculated values for different polymer structures found in ESI-MS spectrum of P1'

Structure	n	Peak in spectrum	Peak calculated
 <p>Na⁺</p> <p>— R = </p>	0	753.67	753.49
	1	1175.67	1175.78
	2	1598.17	1598.06

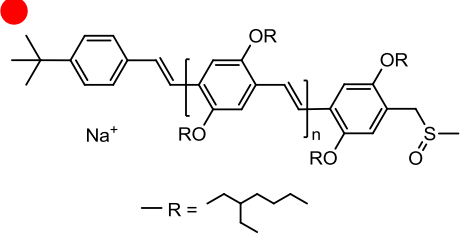
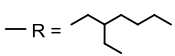
Structure	n	Peak in spectrum	Peak calculated
 <p>Na⁺</p> <p>— R = </p>	1	1013.67	1013.67
	2	1436.33	1435.96
	3	1858.17	1858.24

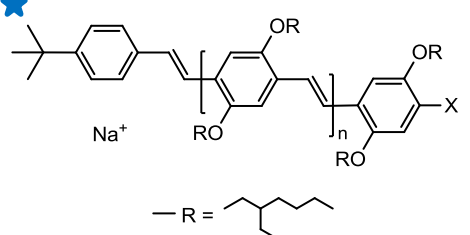
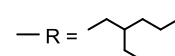
Structure	m	n	Peak in spectrum	Peak calculated
 <p>Na⁺</p>	0	1	1112.50	1111.78
	1	1	1534.33	1534.06
	2	1	1956.25	1956.35
Structure	n	Peak in spectrum	Peak calculated	

◆		899.58	
		1321.33	
		1744.00	

Conjugated polymer with *tert*-butyl initiator (P1)

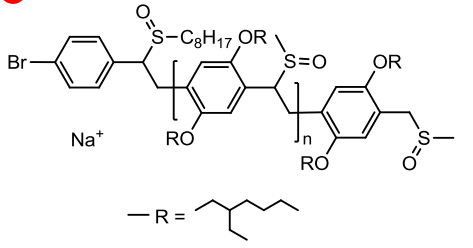
Table S2: Comparison between measured and calculated values for different polymer structures found in ESI-MS spectrum of **P1**

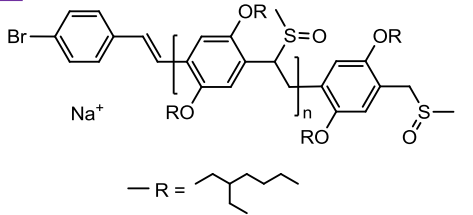
Structure	n	Peak in spectrum	Peak calculated
 <p>Na⁺</p> <p>— R = </p>	1	949.73	949.67
	2	1307.73	1307.96
	3	1666.67	1666.25

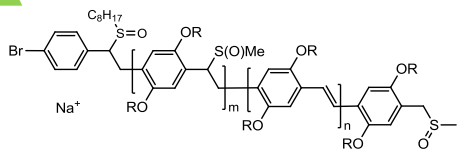
Structure	n	Peak in spectrum	Peak calculated
 <p>Na⁺</p> <p>— R = </p>		863.80	
		1221.87	
		1580.93	
		1938.93	


Precursor polymer with bromine initiator (P2')

Table S3: Comparison between measured and calculated values for different polymer structures found in ESI-MS spectrum of P2'

Structure	n	Peak in spectrum	Peak calculated
	0	777.50	777.34
	1	1199.33	1199.63
	2	1621.33	1621.91

Structure	n	Peak in spectrum	Peak calculated
	1	1037.50	1037.52
	2	1459.17	1459.80
	3	1881.92	1882.09

Structure	m	n	Peak in spectrum	Peak calculated
	0	1	1135.33	1135.63
	1	1	1557.17	1557.91
	2	1	1980.08	1980.20

Structure	n	Peak in spectrum	Peak calculated
		899.67	
		1321.58	
		1744.33	

If a closer look is taken into the unknown mass peaks designated with the orange diamond, clearly no bromine isotope pattern is found. It can thus be concluded that no initiator is present in these polymer chains.

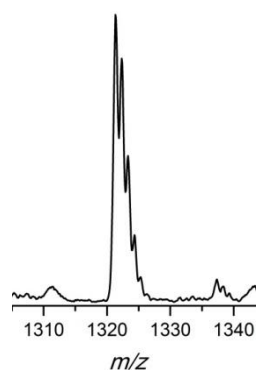


Figure S1: Zoom of mass peak at 1321.58 Da (indicated with orange diamond)

Conjugated polymer with bromine initiator (P2)

Table S4: Comparison between measured and calculated values for different polymer structures found in ESI-MS spectrum of **P2**. Again the values for the most intense peaks are reported.

Structure	n	Peak in spectrum	Peak calculated
	1	973.53	973.52
	2	1331.60	1331.81
	3	1689.67	1690.09
		887.67	
		1245.73	
		1603.87	
		1961.93	

Block copolymer synthesis; $^1\text{H-NMR}$ spectra for initiator **11** and for polymers **P3** and **P4**

$^1\text{H-NMR}$ spectrum for initiator **11**

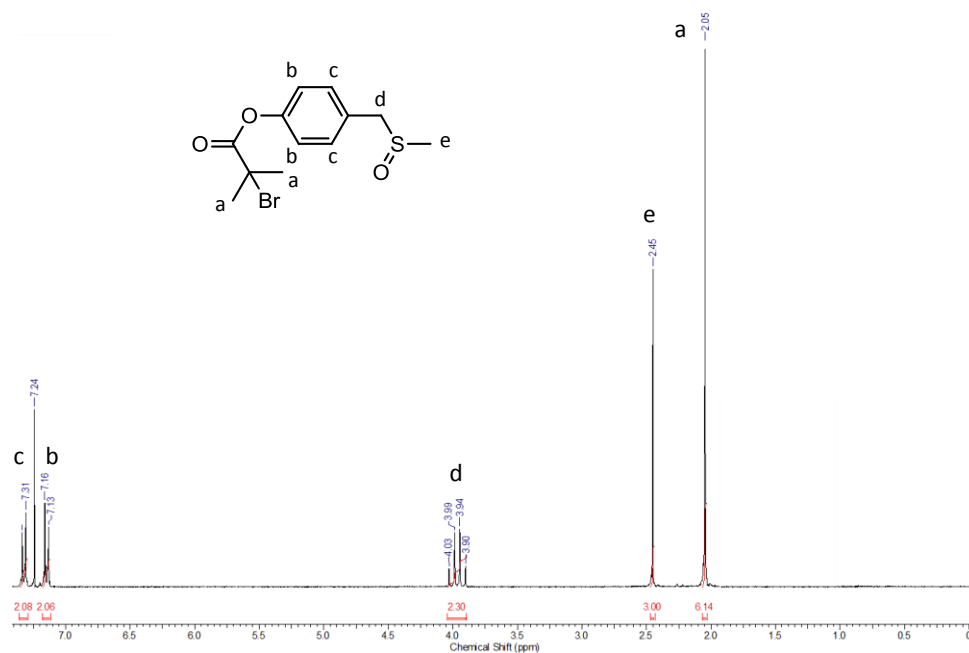


Figure S2: $^1\text{H-NMR}$ spectrum of initiator **11**

$^1\text{H-NMR}$ spectra for BEH-PPV **P3** and BEH-PPV-*b*-P(*t*-BuA) **P4** (50 eq *t*-BuA)

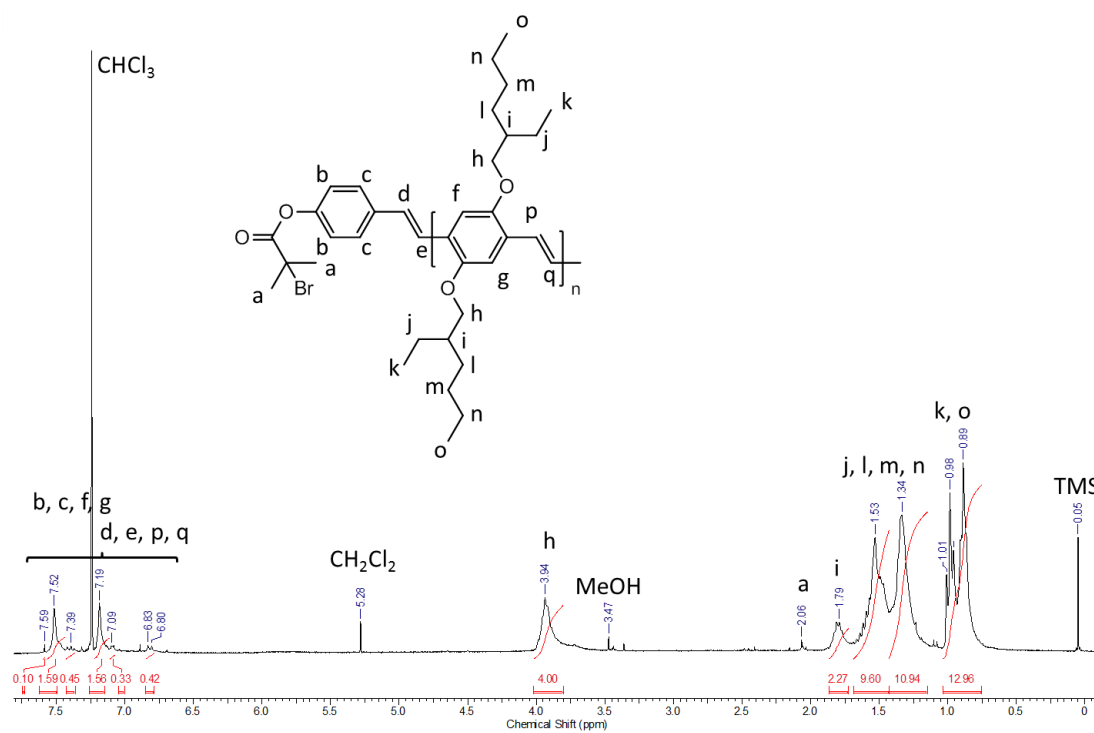


Figure S3: $^1\text{H-NMR}$ spectrum of BEH-PPV **P3**

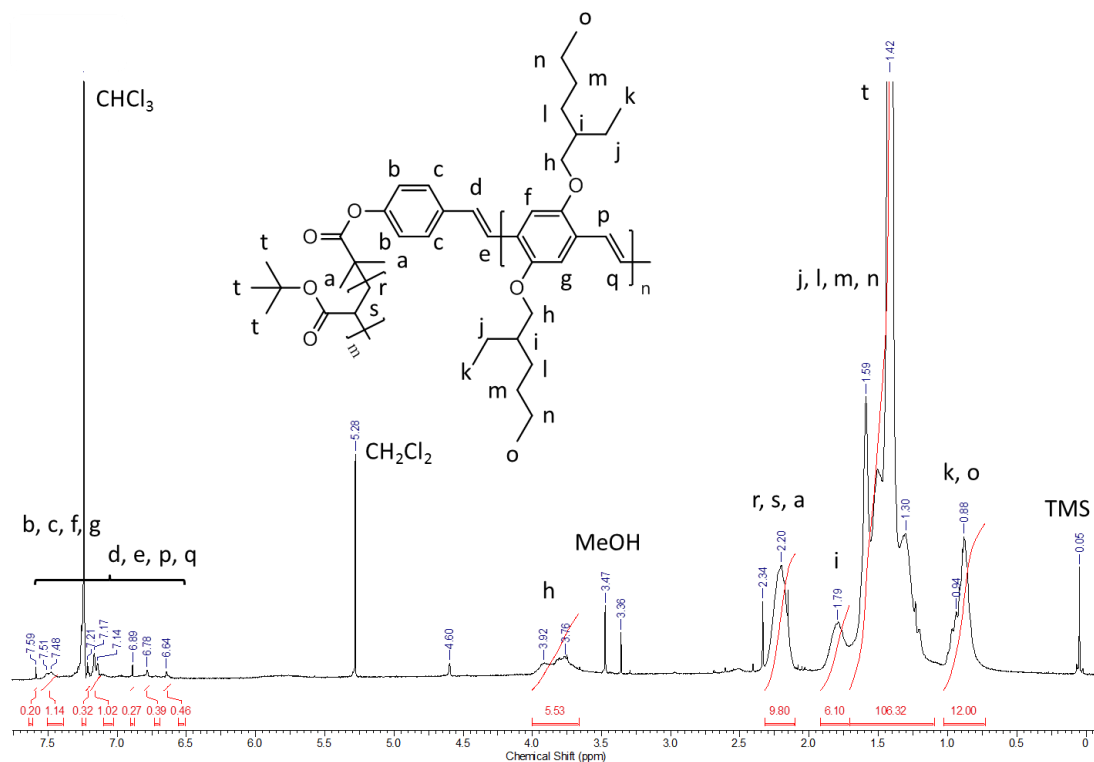


Figure S4: $^1\text{H-NMR}$ spectrum of BEH-PPV-*b*-P(*t*-BuA) **P4**

To check for block lengths for the different polymer blocks in **P4** (synthesized with 50 eq of *t*-BuA), integration of the peaks for signals k and o (for the PPV block) and for r and s (for the acrylate block) were compared. So for one PPV unit, three acrylate units were found. From the M_n of the pure BEH-PPV ($5300 \text{ g}\cdot\text{mol}^{-1}$), it was calculated that 15 PPV units were present. This would mean a presence of 45 acrylate units which translates in a molecular weight of approximately $5700 \text{ g}\cdot\text{mol}^{-1}$. In total this gives an average M_n of $11000 \text{ g}\cdot\text{mol}^{-1}$ which deviates from the measured $6400 \text{ g}\cdot\text{mol}^{-1}$ using GPC (towards PS standards). This difference can be addressed to the difference in hydrodynamic volume, which is very different for the stiff PPV block and the coiled acrylate block.

Block copolymer P4, discussion on UV-detected (λ_{\max}) GPC profiles

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). Analysis of the MWD of the polymer with UV detection at 493 nm 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 an Agilent 1100 DAD UV detector at 60°C. Chlorobenzene (CB) was used as the eluent at a flow rate of 1.0 mL \cdot min⁻¹. Molecular weights were determined relative to polystyrene standards.

Results

To look more closely into the characterization of the block copolymers, UV-Vis spectrometry measurements were done (Figure S2). Here it could be seen that only a very slight difference in λ_{\max} was found for the different block copolymers (493, 493 and 490 nm respectively for 50, 100 and 200 eq *t*-BuA added) compared to the pure PPV (494 nm).

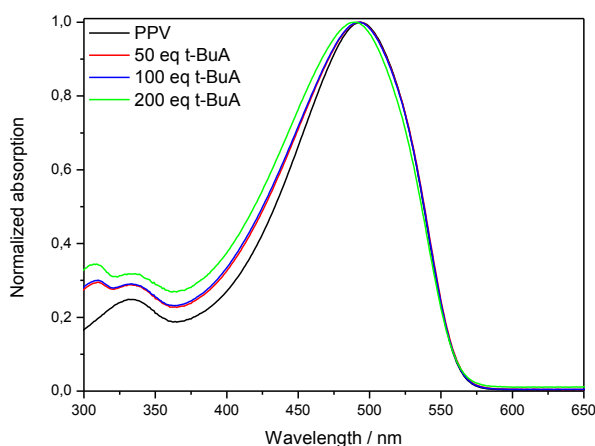


Figure S5: UV-Vis spectra for polymers **P3** and **P4** with different acrylate block lengths

To prove that a block copolymer was indeed synthesized, GPC profiles were measured with detection at λ_{\max} of the polymers (493 nm, only PPV absorption). If a monomodal peak is

found, with comparable molecular weight as for RI detection, it can be concluded that the acrylate is attached to the PPV block and indeed a block copolymer is formed. However, the expected result is not found for the block copolymers (samples measured with chlorobenzene (CB) as the solvent). A monomodal GPC profile is measured and a nice shift in molecular weight is seen with the addition of a higher amount of acrylate to the polymerization reaction (Figure S3, top). If UV detection is used at the maximal wavelength (493 nm) of the polymers (Figure S3, left) and also at the maximal wavelength that was found for a very pure PPV-b-P(t-BuA) block copolymer,ⁱ 465 nm (Figure S3, right), a bimodal profile is observed for the block copolymers. The more acrylate added to the system, the more pronounced the bimodality. It is clear that the low molecular weight peak originates from a pure PPV block (black line), indicating that no complete reinitiation for the SET-LRP occurs. Because only the PPV block absorbs the light at this wavelength, an overestimation is, however, made for the presence of the PPV homopolymer. Quantification of the presence of PPV homopolymer is difficult, because of the difference in signal measured at both wavelengths. When compared to the RI measurements, a nice shift of the monomodal peak is found, indicating a very small PPV homopolymer weight fraction.

With changing the parameters of the reaction (initiator-, ligand, monomer concentrations) it may be possible to overcome this observed bimodality. Also – as we demonstrated in our previous study on block copolymers from consecutive anionic polymerization – the use of recycling preparative GPC can be used to remove the PPV homopolymer. It should be noted though that a further refinement of conditions was so far not required, since the block copolymers show distinct behaviour after hydrolysis of chains and form pH-responsive micelles, which underpins the good structural integrity of the materials.

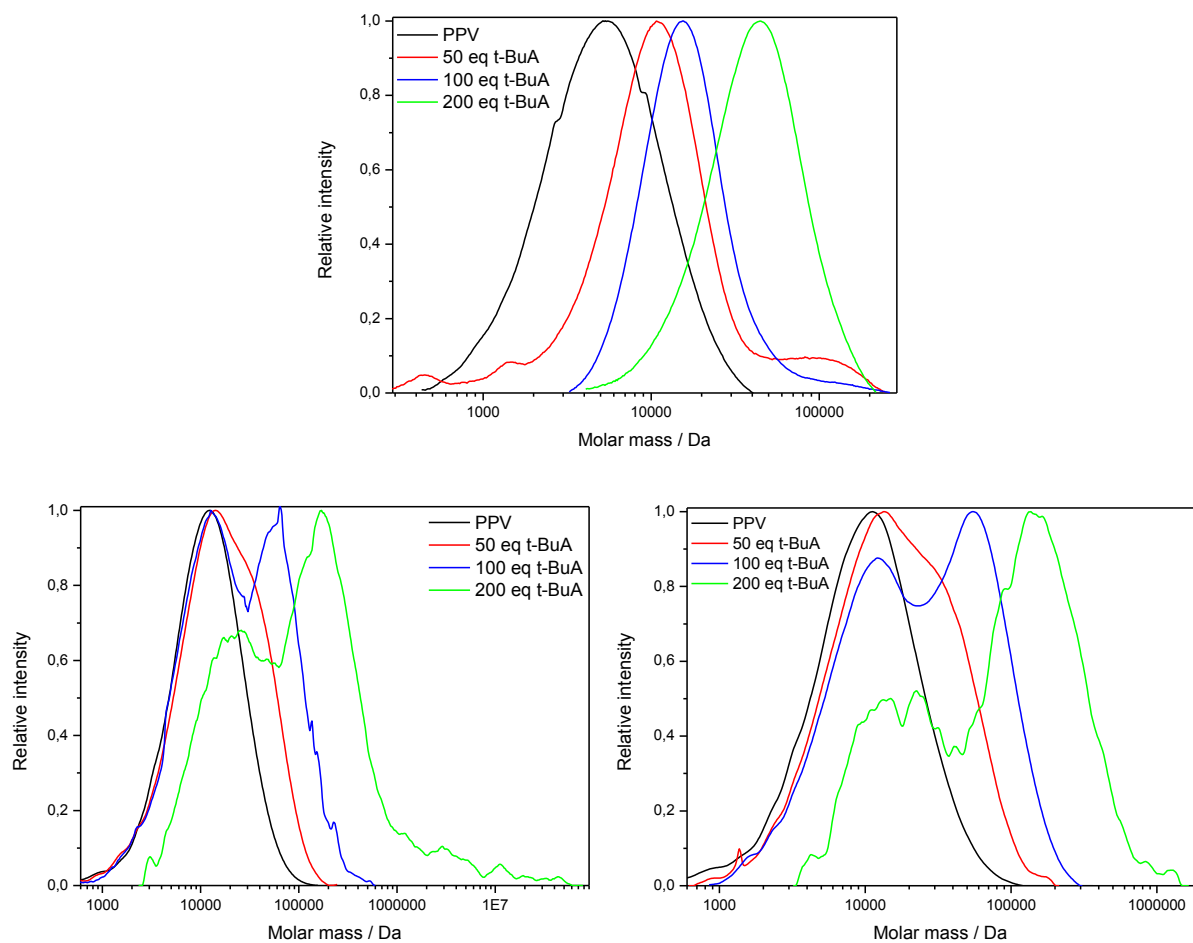


Figure S6: GPC profiles for **P3** and **P4** measured on chlorobenzene GPC with RI (top) and UV (left: 493 nm and right: 465 nm) detection

ⁱ I. Cosemans, J. Vandenberg, V. S. D. Voet, K. Loos, L. Lutsen, D. Vanderzande and T. Junkers, *Polymer*, 2013, **54**, 1298.