Supporting Information to

Controlled Synthesis of MDMO-PPV and Block Copolymers Made Thereof

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1. Experimental Section

1.1. General Data

Unless otherwise stated, all reagents and chemicals were obtained from commercial sources (Acros and Aldrich) and used without further purification. NMR spectra were recorded with a Varian Inova 300 spectrometer at 300 MHz for ^{1}H NMR and at 75 MHz for ^{13}C NMR using a 5 mm probe. Analysis of the MWDs of the polymer samples were performed on a Tosoh EcoSEC operated by PSS WinGPC software, equipped with a PLgel 5.0 µm guard column (50 × 8 mm), followed by three PLgel 5 µm Mixed-C columns (300 × 8 mm) and a differential refractive index detector using THF as the eluent at 40 °C with a flow rate of 1 mL min^{-1}. The SEC system was calibrated using linear narrow polystyrene standards ranging from 474 to 7.5 x 10^{6} gmol^{-1} (PS (K = 14.1 × 10^{-5} dLg^{-1} and α = 0.70), and toluene as a flow marker. FT-IR spectra were collected with a Perkin-Elmer Spectrum One FT-IR spectrometer (nominal resolution 4 cm-1, summation of 16 scans).

1.2. Synthesis

Synthesis of premonomers *2-[(n-Octylsulfinyl)methyl]-5-(chloromethyl)-1-(3,7-dimethyloctyloxy)-4-methoxybenzene (1a)* and *2-[(n-Octylsulfinyl)methyl]-5-(chloromethyl)-4-(3,7-dimethyloctyloxy)-1-methoxybenzene (1b)* was reported elsewhere (Figure 1).[1] All properties were in agreement with the previously reported materials. More information on the isomer mixture can be found in ref.[1]

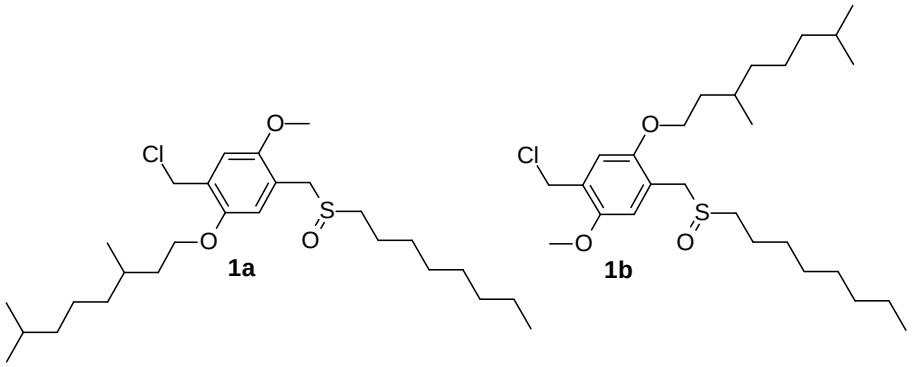

Figure S1. Molecular structures of the alkoxy substituted sulfinyl premonomer **1** (2 isomers).

Synthesis of Br-endcapped MDMO Sulfinyl precursor PPV (2)

A solution of MDMO sulfinyl premonomer **1** (250 mg, 0.51 mmol, 1equiv.) and CBr_4 (1, 2, 4, 8 or 12 equiv.) in 2-butanol (3.7 mL) and a solution of Na*t*BuO (64 mg, 0.67 mmol) in 2-butanol (4.2 mL) were degassed for 1 h at 30 °C by passing through a continuous stream of nitrogen. The base solution was added in one portion to the stirred monomer solution. After 1h, the reaction mixture was quenched in ice water (100 mL). The excess of base was neutralized with HCl (1 M). The aqueous phase was extracted with $CHCl_3$ (3 x 40 mL). After combination of the organic phases and evaporation of the solvent, the obtained crude polymer was again dissolved in $CHCl_3$ (2 mL) and precipitated in stirred cold methanol (100 mL). The mixture was filtered and the polymer was collected and dried *in vacuo*. Yields: 66%–80%; SEC (THF): M_n = 11743 g/mol, PD = 2.0. ^{1}H NMR ($CDCl_3$): 6.90–6.20 (br m, 2H), 4.90/4.60 (br t, 1H), 4.00–2.90 (br m, 7H), 2.70–2.10 (br t, 2H), 1.90–1.10 (br m, 22H), 1.00–0.80 (br m, 12 H); ^{13}C NMR ($CDCl_3$): 151.40, 127.0, 110.50, 67.90, 59.10–55.10, 56.40, 49.70, 39.20, 37.40, 36.60, 32.10–29.10, 30.20, 27.90, 24.60, 22.60, 21.9, 19.80, 13.50.

Thermal Elimination of Br-endcapped MDMO Sulfinyl Precursor Polymer 2 to Conjugated MDMO-PPV (3).

From a solution of **2** (160 mg) in toluene (20 mL) oxygen was removed by purging for 1 h with nitrogen. Subsequently, the solution was heated to 110 °C and stirred for 3 h. Subsequently, the toluene was evaporated and the mixture was re-dissolved in $CHCl_3$ (2mL). After cooling to room temperature, the orange-red solution was precipitated drop wise in cold acetone (100 mL). The polymer was filtered off, washed with cold acetone and dried at room temperature under reduced pressure. The conjugated MDMO-PPV **3** was obtained as a red polymer. Yields were quantitative. SEC (THF): M_n = 22947 g/mol, PD = 1.59. ^{1}H NMR ($CDCl_3$): 7.5 (br, 2H) 7.2 (br, 2H) 4.6–3.2 (br m, 5H) 2.1–0.6 (br m; 19H); ^{13}C NMR ($CDCl_3$): 151.4; 127.0; 123.3; 110.5; 108.8; 67.9; 56.4; 39.2; 37.4; 36.6; 30.2; 27.9; 24.6; 22.6; 19.8; IR (KBr, cm^{-1}): 2957, 2925, 2860, 1510, 1469, 1395, 1217, 1028, 872.

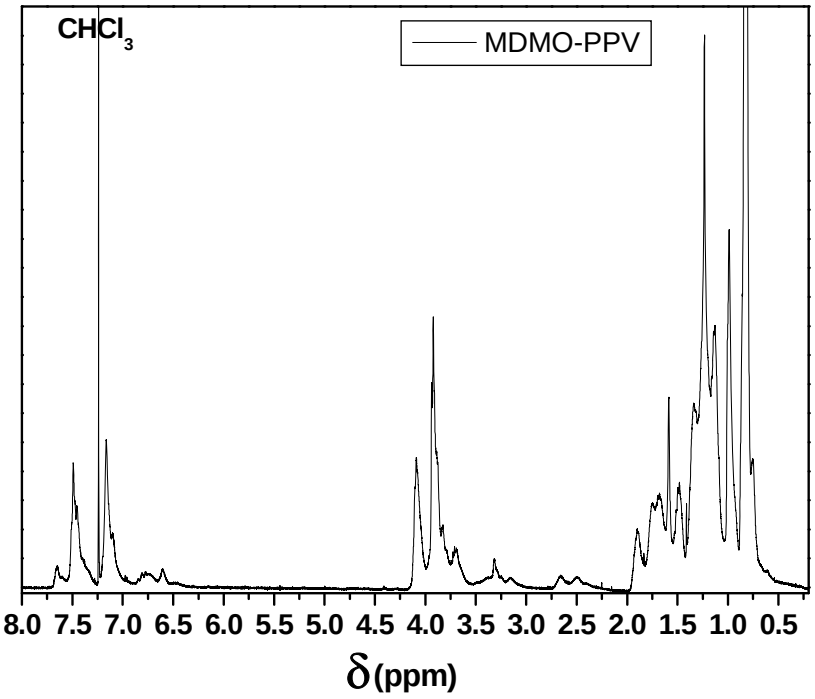

Figure S2. ^{1}H-NMR spectrum of MDMO-PPV **3**.

Chain extension experiment of Br-endcapped MDMO Sulfinyl precursor PPV via ATRP with Styrene (4).

Br-endcapped precursor PPV macroinitiator **2** (100 mg, $8.5*10^{-6}$ mol, 1 equiv.), Cu(I)Br (1.2 mg, $8.5*10^{-6}$ mol, 1 equiv.) and styrene (177 mg, $1.7*10^{-3}$ mol, 200 equiv.) were mixed in a small reaction vial which was placed in an ice bath and purged for 1h with a continuous stream of N_2. PMDETA (4.5 mg, $2.5*10^{-5}$ mol, 3 equiv.) and EtOAc (0.2 mL) were mixed in a second vial and purged for 1h with N_2. The reaction vial was removed from the ice bath and placed in an oil bath of 75 °C. Subsequently the PMDETA/EtOAc mixture was added to the reaction mixture via a N_2 purged syringe. The mixture was stirred for 1h at 75 °C, under N_2 atmosphere. Subsequently, the reaction was quenched by cooling in liquid N_2 and opening to air. The reaction mixture was poured over a small SiO_2 column to remove the Cu(II)Br_2 and dried in a alumina dish. A bright yellow sticky polymer was obtained. SEC (THF): M_n = 12817 g/mol, PD = 2.11.

Thermal Elimination of Br-endcapped MDMO-Precursor-PPV-(co)-Polystyrene block-copolymer 4 to Conjugated MDMO-PPV-(co)-PS block-copolymer (5).

From a solution of **4** (50 mg) in toluene (20 mL) oxygen was removed by purging for 1 h with nitrogen. Subsequently, the solution was heated to 110 °C and stirred for 3 h. Subsequently, the toluene was evaporated and the mixture was re-dissolved in $CHCl_3$ (2mL). After cooling to room temperature, the orange-red solution was precipitated drop wise in cold acetone (100 mL). The

polymer was filtered off, washed with cold acetone and dried at room temperature under reduced pressure. The conjugated MDMO-PPV-(co)-PS block copolymer **5** was obtained as a red polymer. Yields were quantitative. SEC (THF): M_n = 27563 g/mol, PD = 1.64. It should be noted that the reduction in PDI after elimination is in all likelihood due to partial fractionation of polymer distribution. The change in M_n is a well known effect stemming from the change in hydrodynamic volume and does not constitute a true change in the average chain length.

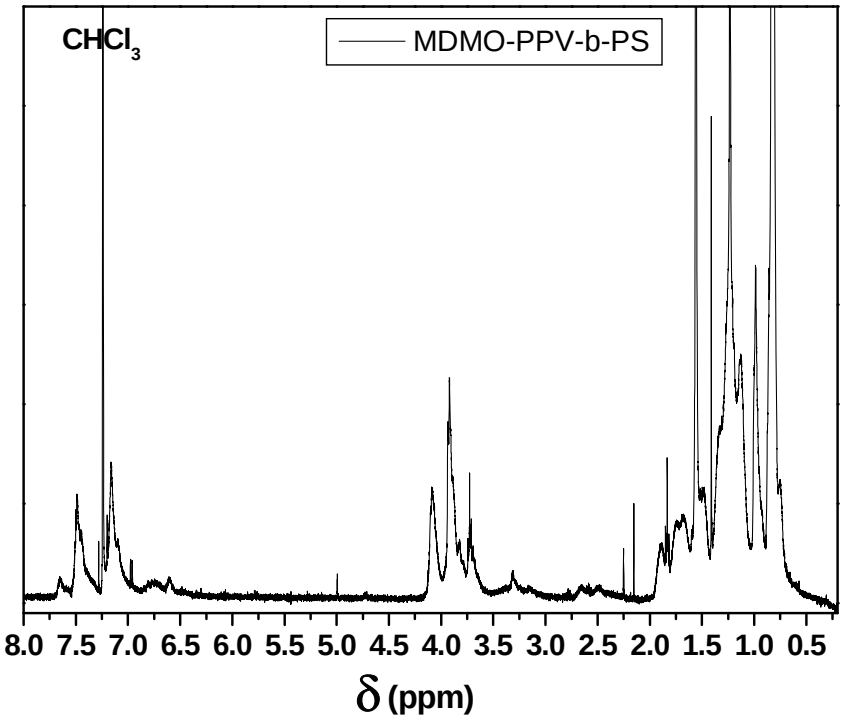

Figure S3. ^{1}H-NMR spectrum of MDMO-PPV-*b*-PS **5**.

Comparison of NMR spectra

Both NMR spectra are – despite the chain extension with polystyrene – quite similar. No significant change in the spectra is seen due to overlap of the specific peak regions. Backbone-peaks of PPV and PS occur in the same reagion and my not be separated from each other. Also, in the aromatic region, substantial overlap exists. Closer inspection reveals, however, an increase of the integral of the aromatic region (excluding the $CHCl_3$ peak) by 21 % when both spectra are normalized on the peak region of the OC1C10-substituents (3.5-4.25 ppm), which are specific for MDMO-PPV and not overlapped with PS. Thus, the NMR spectra are in agreement with the chain extension seen in GPC.

References:

(1) L. J. Lutsen, A. J. van Breemen, Willi Kreuder, Dirk J. M. Vanderzande, Jan M. J. V. Gelan, *Helvetica Chimica Acta* **2000**, *83*, 3113–3121.

(2) H. Roex, P. Adriaensens, D. Vanderzande, J. Gelan, *Macromolecules* **2003**, *36,* 5613–5622.