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## ARTICLE

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# Synthesis of polymer precursors of electro-active materials by SET-LRP

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#### **Experimental**

#### Materials

Copper wire (diameter = 0.25 mm) was pretreated by washing in hydrochloric acid for 15 min and rinsed thoroughly with Milli-Q water, dried under nitrogen and used immediately. DCM was distilled over CaH<sub>2</sub>. Trietylamine was distilled over KOH pellets. CuBr<sub>2</sub> (Acros, 99+%) 2,2,6,6-tetramethylpiperidin-4-yl methacrylate (**TMPM**, TCl), N,N,N',N',Pentamethyldiethylenetriamine (PMDETA, Aldrich, 98%), ethyl- $\alpha$ -bromoisobutyrate (EBiB, Acros, 98%) 2-propyl alcohol (**IPA**, Acros, 99%), 3-choloropropanol (Acros, 98%), sodium azide (NaN<sub>3</sub>, Aldrich, 99.99%), methacryloyl chloride (Acros, 95%), benzyl alcohol (Aldrich, 99%),  $\alpha$ -bromoisobutyryl bromide (Aldrich, 98%) 4-hydroxy-2,2,6,6-tetramethyl-piperidineoxy (Acros, 98%), trimethylacetyl chloride (Acros, 99%) and all other chemicals were used as received.

#### Instrumentation

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were acquired either on a 300 MHz Bruker Avance II or on a 500 MHz Bruker Avance II in deuterated chloroform. Number average molar masses ( $M_n$ ), weight average molar masses ( $M_w$ ), and polydispersity indices (D) of the polymers were measured on an Agilent gel permeation chromatography (GPC) system equipped with an Agilent 1100/1200 pump (25°C; eluent: chloroform/triethylamine/2-propanol 94:4:2; flow rate: 1 mL/min), an Agilent differential refractometer. UV-visible spectra were recorded on a Varian spectro-photometer (Cary, 50 Conc). Infrared (FT-IR) spectra were recorded on thin films deposited onto sodium chloride plates with a FT-IR spectrometer (Shimadzu FTIR-8400S). Cyclic voltammetry was performed using an Arbin Instruments Battery Tester, BT-2043 and a CHI660B instrument. (scan rate: 0.1 mV s<sup>-1</sup>).

#### Synthesis of 3-azido propanol

3-Chloropropanol (22.1 mL, 25.0 g, 0.264 mol, 1 eq.) was added to a mixture of water (40 mL), sodium azide (34.4 g, 0.529 mol, 2 eq.), and tetrabutylammonium bromide (1 g, 0.003 mol, 0.012 eq.). The mixture was stirred at 80 °C for 24 h and then at room temperature for 16 h. The product was extracted with ether three times, the organic phase was dried over MgSO<sub>4</sub>, the solution was concentrated and 3-azido propanol was distilled under vacuum (yield: 23.5 g, 88%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 3.76 (t, 2H, CH<sub>2</sub>.O), 3.46 (t, 2H, CH<sub>2</sub>N<sub>3</sub>), and 1.84 (t, 2H, C-CH<sub>2</sub>.C).

#### Synthesis of 3-azidopropyl methacrylate

A solution of 3-azidopropanol (16.4 g, 0.162 mol, 1 eq.), triethylamine (26.0 mL, 0.187 mol, 1.15 eq.) and  $CH_2Cl_2$  (140 mL) was cooled in an ice-water bath. A solution of methacryloyl chloride (17.5 mL, 0.179 mol, 1.1 eq.) in  $CH_2Cl_2$  (20 mL) was added dropwise over a period of 30 min. The mixture was slowly brought to 20°C and stirred overnight. The mixture was extracted successively with an aqueous solution of hydrochloric acid (0.1M), a saturated solution of NaHCO<sub>3</sub>, and water. The organic phase

was dried over MgSO<sub>4</sub>. The solution was concentrated and 3-azidopropyl methacrylate was purified by column chromatography on SiO<sub>2</sub> (eluent: petroleum ether/ethyl acetate 95:5).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 6.11 (m, 1H, =CH), 5.58 (m, 1H, =CH), 4.24 (t, 2H, CH<sub>2</sub>-O), 3.52 (t, 2H, CH<sub>2</sub>-N<sub>3</sub>) and 1.91-2.02 (m, 5H, overlapping CH<sub>3</sub>-C and C-CH<sub>2</sub>-C).

#### Synthesis of benzyl-2-bromoisobutyrate

A solution of benzyl alcohol (2.00 mL, 0.019 mol, 1 eq.), triethylamine (2.96 mL, 0.021 mol, 1.1 eq.) and  $CH_2Cl_2$  (15 mL) was cooled in an ice-water bath. A solution of  $\alpha$ -bromoisobutyryl bromide (2.63 mL, 0.021 mol, 1.1 eq.) in  $CH_2Cl_2$  (4 mL) was added dropwise over a period of 30 min. The mixture was slowly brought to 20°C and stirred overnight. The mixture was extracted successively with an aqueous solution of hydrochloric acid (0.1M), a saturated solution of NaHCO<sub>3</sub>, and water. The organic phase was dried over MgSO<sub>4</sub>. The solution was concentrated and the benzyl-2-bromoisobutyrate was purified by vacuum distillation (yield: 4.75, 95%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 6.11 (m, 1H, =CH), 5.58 (m, 1H, =CH), 4.24 (t, 2H, CH<sub>2</sub>-O), 3.52 (t, 2H, CH<sub>2</sub>-N<sub>3</sub>) and 1.91-2.02 (m, 5H, overlapping CH<sub>3</sub>-C and C-CH<sub>2</sub>-C).

#### Synthesis of 2,2,6,6-tetramethyl-piperidineoxy tert-butyrate (TEMPO-tBu)

A solution of 4-hydroxy-2,2,6,6-tetramethyl-piperidineoxy (1.02 g, 5.89 mmol, 1 eq.), triethylamine (0.9 mL, 6.49 mmol, 1.11 eq.) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was cooled in an ice-water bath. A solution of trimethylacetyl chloride (0.8 mL, 6.49 mmol, 1.1 eq.) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added dropwise over a period of 30 min. The mixture was slowly brought to 20 °C and stirred overnight. The mixture was extracted with water three times. The organic phase was dried over MgSO<sub>4</sub>. The solution was concentrated and the TEMPO-tBu was purified by column chromatography on SiO<sub>2</sub> (eluent: petroleum ether/ethyl acetate 95:5 ; yield: 535 mg, 35%). FT-IR (cm<sup>-1</sup>): 1720 (C=O), 1481 (C-O) 1350 (N-O); MS (ESI): m/z = 258.2 ([M+2H]<sup>2+</sup>, 20), 257.1 ([M], 27), 256.1 ([M], 100), 154 ([C<sub>9</sub>H<sub>16</sub>NO], 21), 85 ([C<sub>5</sub>H<sub>9</sub>O], 6)

#### Results

Synthesis of the PTMPM



Figure S1: GPC chromatogram of PTMPM synthesised by SET-LRP



Figure S2: Evolution of the GPC chromatograms with the polymerisation time for the kinetic experiment.

#### Investigation of the ω chain-end



#### Synthesis of the electro-active PTMA

UV-Vis spectroscopy was used to determine the degree of oxidation of the PTMA. The UV-Vis spectra of solutions of PTMA (C = 5 and 10 g/L in polymer) in CH<sub>2</sub>Cl<sub>2</sub> are shown in Figure S3 left. The maximum of absorbance ( $\lambda_{max} = 464$  nm) was measured and compared to a TEMPO *tert*-butyrate calibration (dashed black line in Figure S3 right).



Figure S4: Determination of the oxidation degree by UV-Vis analysis.



Figure S5: Overlay of the GPC chromatograms of PTMPM (black curve) and PTMA (red curve).