

Supplementary Information

Synthesis and solvent-free polymerisation of vinyl terephthalate for application as anode material in organic batteries

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1. General remarks

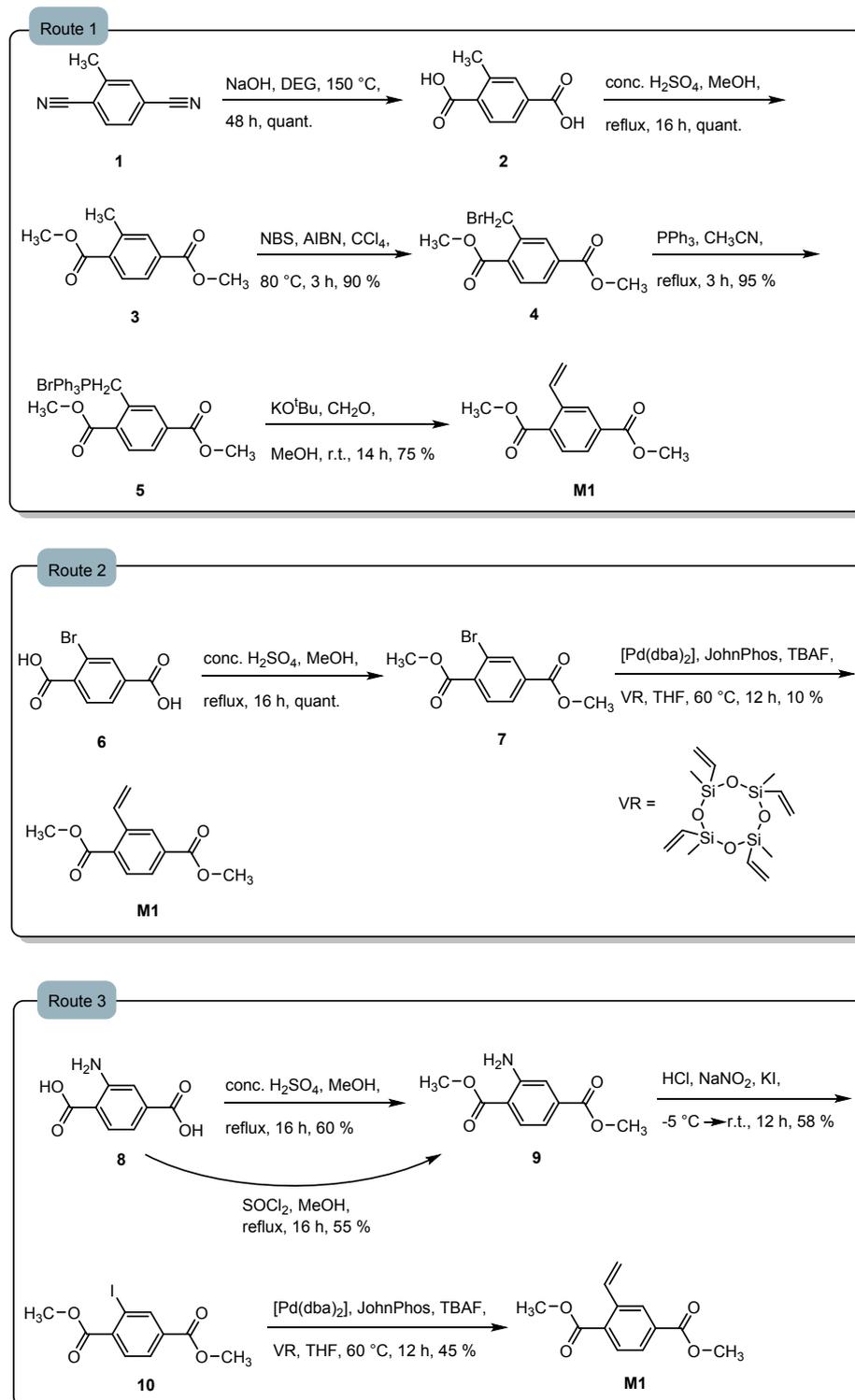
NMR spectra were recorded on a *Bruker* AMX 500 (^1H NMR: 500 MHz, ^{13}C NMR: 125 MHz) or an *Avance* 400 spectrometer (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz), normally at 25 °C. Chemical shift values (δ) are expressed in parts per million using solvent (^1H NMR, $\delta_{\text{H}} = 7.26$ and ^{13}C NMR, $\delta_{\text{C}} = 77.0$ for CDCl_3 ; ^1H NMR, $\delta_{\text{H}} = 2.50$ and ^{13}C NMR, $\delta_{\text{C}} = 39.52$ for DMSO-d_6) as internal standard. Melting points were determined using a *Büchi* M-565. Elemental analyses were performed on an *Elementar Vario* EL (Ulm University). Cyclic voltammetry experiments were performed with an *Autolab* Potentiostat Galvanostat in a three-electrode single-compartment cell with a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. All potentials were internally referenced to the ferrocene/ferricenium couple Fc/Fc^+ . FT-IR spectra were measured with a *Perkin Elmer* Spectrum 2000. MS/CI experiments were performed using a *Finnigan* MAT, SSQ-7000 spectrometer.

2. Chemicals

Methylterephthalonitrile **1** and 2-bromoterephthalic acid **6** were purchased from *Sigma Aldrich*. 2-Aminoterephthalic acid was provided from *Acros Organics* and 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane was purchased from *abcr GmbH & Co KG*. Solvents were purchased from *Merck and Sigma Aldrich*, purified and dried by standard methods prior to use. Compounds **1-10** as well as **M1** are literature-known, however, in some cases the synthesis procedure and/or a proper characterisation is missing, hence, they are given here.

3. Overview of different routes for the synthesis of M1.

Monomer Syntheses



Scheme 1: Overview of three different routes for the synthesis of **M1**.

4. Synthesis and characterisation

2-Methylterephthalic acid (2):ⁱ

To a solution of NaOH (3.38 g, 84 mmol) dissolved in 30 ml diethylene glycol and a few drops demin. water were added 2-methylterephthalonitrile (3 g, 21 mmol). The reaction mixture was heated to 150 °C for 48 h. After cooling down to room temperature the mixture was acidified to pH 1 using 2N HCl. The resulted precipitate was collected and washed with ethanol. After drying under vacuum the product was obtained as a colourless solid in almost quantitative yield (3.70 g).

¹H-NMR (DMSO-d₆ – 400MHz, ppm): δ = 7.72 (s, 1H), 7.70 (d, 1H, *J* = 18 Hz), 7.63 (d, 1H, *J* = 18 Hz), 2.48 (s, 3H); ¹³C-NMR (DMSO-d₆ – 400MHz, ppm): δ = 170.79, 168.50, 136.47, 131.53, 128.74, 126.19, 20.99.

Dimethyl 2-methylterephthalate (3):ⁱⁱ

5 ml of conc. H₂SO₄ were added to a solution of 3 g (17 mmol) 2-methylterephthalic acid dissolved in 30 ml MeOH and heated to reflux for 16 h. After cooling to room temperature the solution was neutralised with saturated NaHCO₃ and the white precipitate was collected, washed with water and dried under vacuum. The product was obtained as a colourless solid in almost quantitative yield (3.43 g).

¹H-NMR (CDCl₃ – 400MHz, ppm): δ = 7.96-7.90 (m, 2H), 7.88 (d, 1H, *J* = 13 Hz), 3.93 (s, 3H), 3.91 (s, 3H), 2.63 (s, 3H); ¹³C-NMR (CDCl₃ – 400MHz, ppm): δ = 167.46, 166.43, 140.16, 133.56, 132.77, 132.62, 130.51, 126.71, 52.39, 52.17, 21.55.

Dimethyl 2-(bromomethyl)terephthalate (4):ⁱⁱ

A mixture of dimethyl 2-methylterephthalate (2 g, 9.61 mmol) and NBS (2.05 g, 11.53 mmol) in 15 ml CCl₄ was heated to reflux and 30 mg (0.19 mmol) of AIBN was added. After 3 h the mixture was cooled to room temperature, washed with water and brine and the organic phase concentrated at rotary evaporator. The product was obtained after column chromatography (silica, hexane/ethyl acetate 4:1) as a colourless solid with a yield of 90 % (2.48 g).

¹H-NMR (CDCl₃ – 400MHz, ppm): δ = 8.12 (t, 1H, *J* = 2.5 Hz), 7.98 (m, 2H), 4.95 (s, 2H), 3.96 (s, 3H), 3.94 (s, 3H); ¹³C-NMR (CDCl₃ – 400MHz, ppm): δ = 165.85, 165.25, 135.07, 134.45, 134.35, 134.21, 133.88, 133.83, 131.66, 131.05, 130.95, 130.19, 130.07, 129.62, 117.91, 117.03, 52.72, 52.47, 29.927, 28.80.

Dimethyl 2-((bromotriphenylphosphanyl)methyl)terephthalate (5):ⁱⁱ

Dimethyl 2-(bromomethyl)terephthalate (2 g, 6.97 mmol) was dissolved in 30 ml acetonitrile and 1.83 g (6.97 mmol) triphenylphosphine was added. The solution was heated to reflux for 3 h. After cooling to room temperature the precipitate was collected, washed with diethylether and dried under vacuum. The product was obtained as a colourless solid in 95 % (3.6 g).

¹H-NMR (CDCl₃ – 400MHz, ppm): δ = 8.12 (s, 1H), 7.98 (dt, 1H, *J* = 1.90 Hz, 4.20 Hz), 7.90 (d, 1H, 8.1 Hz), 7.82-7.72 (m, 3H), 7.65-7.57 (m, 12H), 6.00 (d, 2H, *J* = 15.3 Hz), 3.82 (s, 3H), 3.51 (s, 3H); ¹³C-NMR (CDCl₃ – 400MHz, ppm): δ = 166.62, 165.88, 139.70, 133.74, 133.14, 132.80, 131.60, 129.61, 52.89, 52.82, 30.91. ³¹P-NMR (CDCl₃ – 400MHz, ppm): δ = 24.53.

Dimethyl 2-vinylterephthalate (M1)ⁱⁱⁱ

In a flame dried three-necked round bottom flask with a gas inlet tube, 3 g (5.46 mmol) of **5** was placed and dissolved in dry methanol. 1.23 g (10.92 mmol) of potassium *tert*-butoxide dissolved in dry methanol (10 ml) was added and the colour of the solution turned to red. After 1 h, in a separate two-necked round bottom flask *para*-formaldehyde was placed and heated to 200 °C which sublimed to formaldehyde gas. The obtained formaldehyde gas was directed with argon flow to the first reaction flask through the gas inlet tube. After all *para*-formaldehyde was sublimed the mixture was stirred for 14 h at room temperature, while the red mixture in the first flask turned to yellow. The mixture was extracted with dichloromethane, washed with water and brine. The organic phases were collected, dried over Na₂SO₄ and filtered. After removal of the solvent under reduced pressure a pale yellow solid was obtained. The product was obtained by sublimation at a cold finger (75 torr, 80 °C) as a colourless solid in 75 % yield (0.90 g).

¹H-NMR (CDCl₃ – 400MHz, ppm): δ = 8.24 (s, 1H), 7.99-7.86 (m, 2H), 7.41 (dd, 1H, *J* = 11.2 Hz, 6.4 Hz), 5.76 (d, 1H, *J* = 17.2 Hz), 5.43 (d, 1H, *J* = 10.7 Hz), 3.95 (s, 3H), 3.92 (s, 3H); ¹³C-NMR (CDCl₃ – 400MHz, ppm): δ = 167.25, 166.24, 139.53, 134.80, 133.11, 132.31, 130.37, 128.32, 128.10, 117.77, 52.48, 52.43. FT-IR (KBr, 25 °C, cm⁻¹): γ = 2927, 1698, 1565, 1489, 1415, 1303, 1265, 922, 788, 763, 751. MS/CI(+) *m/z* = 221; mp = 55 °C. Elemental Analysis: C₁₂H₁₂O₄ (theoretical); C: 65.45; H: 5.49; C₁₂H₁₂O₄ (found); C: 65.72; H: 6.18.

Dimethyl 2-bromoterephthalate (6):^{iv}

2 g (8.16 mmol) 2-bromoterephthalic acid was dissolved in 20 ml methanol and 3 ml conc. H₂SO₄ were added to the solution. The solution was heated to reflux for 16 h. After cooling to room temperature sat. NaHCO₃ was added until neutral and the precipitate was collected, washed with water and dried under vacuum. The product was obtained as a colourless solid in almost quantitative yield (2.21 g).

¹H-NMR (CDCl₃ – 400MHz, ppm): δ = 8.30 (d, 1H, J = 8.4 Hz), 7.99 (dd, 1H, J = 9.6 Hz, 1.6 Hz), 7.80 (d, 1H, J = 1.6 Hz), 3.95 (s, 3H), 3.94 (s, 3H); ¹³C-NMR (CDCl₃ – 400MHz, ppm): δ = 166.32, 165.17, 136.28, 135.38, 133.88, 131.21, 128.28, 121.64, 52.98, 52.90.

Dimethyl 2-aminoterephthalate (6):^v

2-Aminoterephthalic acid (3 g, 16.56 mmol) was mostly dissolved in 30 ml MeOH and while stirring H₂SO₄ was added dropwise. The mixture was then heated to reflux overnight. After cooling down to room temperature saturated NaHCO₃ was added slowly to the solution until the resulting mixture was neutral. The colourless solid was then filtered and washed carefully with water. After drying under vacuum the product was obtained as a colourless solid in 60 % yield (2.08 g).

¹H-NMR (CDCl₃ – 400MHz, ppm): δ = 7.89 (d, 1H, J = 1.6 Hz), 7.80 (d, 1H, J = 8.2 Hz), 7.23 (dd, 1H, J = 6.7 Hz, 1.6 Hz), 5.83 (s, 2H), 3.89 (s, 3H), 3.88 (s, 3H); ¹³C-NMR (CDCl₃ – 400MHz, ppm): δ = 167.99, 166.43, 149.19, 134.35, 131.21, 117.83, 116.54, 113.64, 52.48, 51.90.

Dimethyl 2-iodoterephthalate (6):^{vi}

Dimethyl 2-aminoterephthalate (4 g, 19.12 mmol) was stirred in 2N HCl until most of it was dissolved. Then, the mixture was cooled to 0 °C and 1.58 g (22.94 mmol) NaNO₂ dissolved in 5 ml demin. water was dropped slowly to the mixture. The resulting red mixture was stirred for 2 h at 0 °C. Then, a cold solution of 4.76 g (28.68 mmol) KI in water was given slowly to the red mixture and stirred for 12 h at room temperature. After the addition a yellow suspension was developed which after a while turned to a yellow solution. The solution was extracted from ethyl acetate, washed with NaHSO₃, water and brine, and the organic phase was dried over Na₂SO₄. After a short plug (silica, hexane) and removal of the solvent a yellow solid was obtained which was recrystallised from MeOH to give the product as a pale yellow solid in 58 % yield (3.55 g).

¹H-NMR (CDCl₃ – 400MHz, ppm): δ = 8.62 (s, 1H), 8.04 (d, 1H, J = 8.8 Hz), 7.81 (d, 1H, J = 8.8 Hz), 3.96 (s, 3H), 3.94 (s, 3H);

Dimethyl 2-vinylterephthalate (**M1**)^{vii}

2-Bromoterephthalate (4.5 g, 16.48 mmol) together with [Pd(dba)₂] (190 mg, 0.33 mmol), JohnPhos (200 mg, 0.66 mmol) and tetrabutylammonium fluoride (4.74 g, 18.13 mmol) were placed in a flask and subjected three times to an evacuation-argon-purge cycle. Then, dry THF was added and the red mixture was heated to 60 °C followed by the addition of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (5.98 g \pm 6 ml, 17.36 mmol) was added. After 5 h half of the siloxane amount was again added to the mixture and stirred for 7 h. When TLC showed no additional conversion the mixture was cooled down to room temperature and extracted with diethylether and washed with water and brine, dried over Na₂SO₄ and filtered. After the solvent was removed under reduced pressure the product was obtained by column chromatography (silica gel; hexane/ethyl acetate 3:1) as a colourless solid in 10 % (360 mg).

The same procedure was applied on 2-iodoterephthalate. Yield: 45 %.

¹H-NMR (CDCl₃ – 400MHz, ppm): δ = 8.24 (s, 1H), 7.99-7.86 (m, 2H), 7.41 (dd, 1H, J = 11.2 Hz, 6.4 Hz), 5.76 (d, 1H, J = 17.2 Hz), 5.43 (d, 1H, J = 10.7 Hz), 3.95 (s, 3H), 3.92 (s, 3H); ¹³C-NMR (CDCl₃ – 400MHz, ppm): δ = 167.25, 166.24, 139.53, 134.80, 133.11, 132.31, 130.37, 128.32, 128.10, 117.77, 52.48, 52.43.

Polymerisation of **M1**

In a flame-dried Schlenk tube with a stir bar and under argon atmosphere 300 mg (1.36 mmol) of **M1** was placed and the tube was heated to 80 °C while **M1** was melted. 0.2 mol % (4 mg) of 2,2'-azobis(2-methylpropionitrile) was added to the molten **M1** and stirring was continued. After 30 min a resin was obtained and stirring was not possible any more. The temperature was increased to 150 °C and the tube was maintained at this temperature for 24 h. After cooling to room temperature the yellow solid was transferred into 50 ml MeOH. A colourless precipitate was formed immediately which was subjected to Soxhlet extraction with MeOH overnight. The obtained polymer was dried under vacuum and gave the product in 80 % (240 mg) as a colourless solid.

¹H-NMR (CDCl₃ – 400MHz, ppm): δ = 7.91-7.00 (3H), 4.01-3.51 (3H), 3.50-2.78 (3H), 1.98-1.00 (3H); FT-IR (KBr, 25 °C, cm⁻¹): ν = 2953, 2916, 2848, 1723, 1435, 1286, 1240, 1192, 1116, 753.

Synthesis of P1-Li using LiOH

200 mg (0.91 mmol) of **P1** was dissolved in a mixture of 15 ml THF/H₂O (3:1) and LiOH dissolved in demin. water was added to the solution. This solution was heated to 70 °C and stirred for 14 h. A precipitate was formed. After cooling to room temperature the content of the flask was dropped into a flask with 50 ml THF. A white precipitate was formed which was collected by centrifugation. The precipitate was dissolved in water and given again dropwise to 30 ml THF. The formed precipitate was collected again and the procedure was repeated twice. After drying under vacuum the product was obtained as a pale yellow powder in 50 % (93 mg).

FT-IR (KBr, 25 °C, cm⁻¹): ν = 1517, 1428, 864, 500.

Synthesis of P1-COOH

300 mg **P1** was dissolved in a mixture of 15 ml THF/MeOH (2:1) and 220 mg (4 eq.) NaOH was added to the solution. The mixture was heated to reflux for 14 h. A precipitate was formed which was collected and washed excessively with MeOH. The product was obtained after drying under vacuum as a colourless powder in 80 % yield (210 mg).

NMR measurements did not result in convenient spectra.

FT-IR (KBr, 25 °C, cm⁻¹): ν = 2200-3500, 1702, 1568, 1495, 1419, 1233, 1125, 1054, 916, 880, 853, 757.

Synthesis of P1-Li using LiHMDS

200 mg (1.0 mmol) **P1-COOH** was dissolved in 20 ml dry THF and 700 mg (4.2 mmol) lithium hexamethyldisilazide was added in portions. Then the mixture was heated to 60 °C for 14 h. The formed precipitate was collected and washed with hot THF. The product was obtained after drying under vacuum as a pale yellow powder in 70 % yield (150 mg).

NMR measurements did not result in convenient spectra.

FT-IR (KBr, 25 °C, cm⁻¹): ν = 1517, 1428, 864, 500.

5. Comparison of the IR-spectra of P1-Li obtained via different routes

Figure 1 shows the IR spectra of **P1-Li** obtained *via* treatment with LiOH (middle) or LiHMDS (bottom). The spectra are almost identical which indicates that both routes lead to the same result. For comparison, the IR spectrum of the ester-polymer **P1** is also given (top).

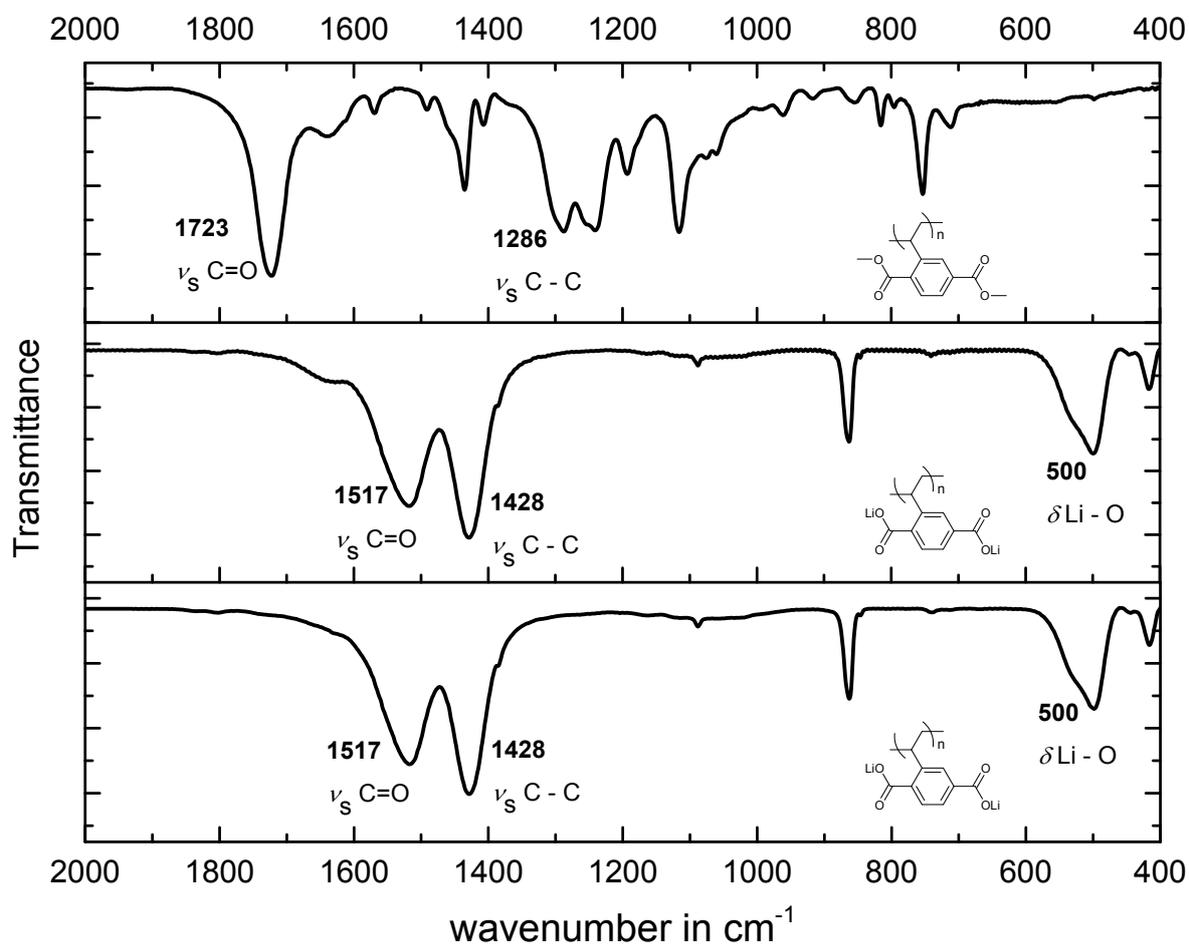


Figure 1: IR-spectra from **P1** (top) and the corresponding **P1-Li** obtained via treatment with LiOH (middle) or LiHMDS (bottom).

6. Comparison of solution-based CVs of the polymers

Polymers with two different molecular weights, 200 kDa and 18 kDa, respectively, have been investigated electrochemically. The cyclic voltammetry investigations were performed under the same conditions as given in General remarks. Comparison of cyclic voltammograms revealed that the chain length did not influence the redox potential of the molecule (Figure 2). This was the case when comparing the monomer with the low molecular weight polymer (18 kDa). In addition, in both cases the drop of current at about -2.50 V vs Fc^+/Fc is observed while the effect in case of the polymer with the higher molecular weight (left) is more pronounced.

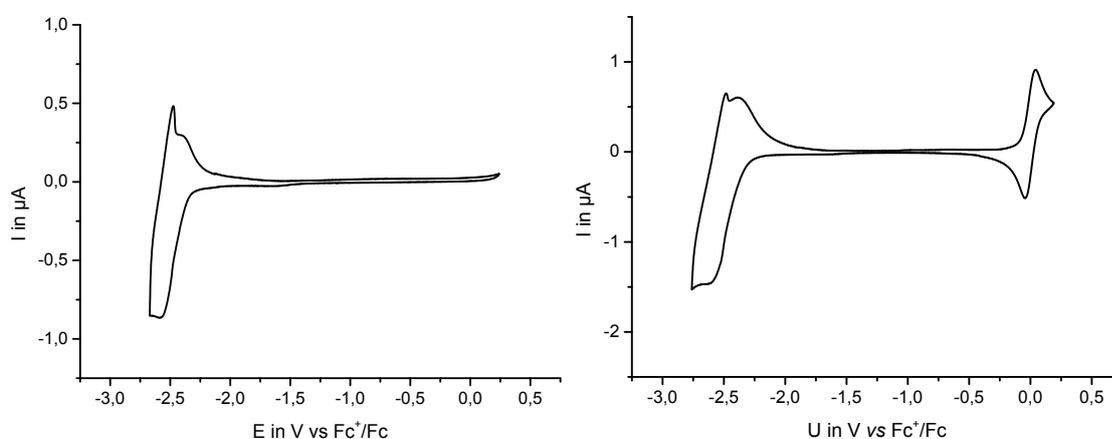


Figure 2: CVs of **P1** with different molecular weights: 200 kDa (left) and 18 kDa (right), respectively.

7. Comparison of CVs of P1-Li and dilithium terephthalate

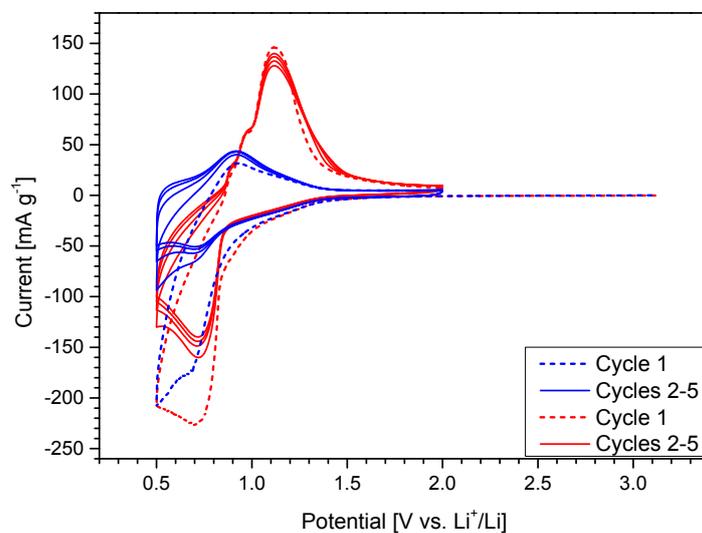


Figure 3: CV of **P1-Li** (blue) compared to dilithium terephthalate (red) in 1 M LiPF_6 / EC:DMC (1:1 by wt.) of electrodes containing active material (56.6 wt. %), PTFE (10.4 wt. %) and carbon black (33 wt. %); 0.1 mV s^{-1} , 5 cycles (cycle 1: dashed lines; cycles 2 - 5: solid lines).

8. Rate capability of P1-Li and dilithium terephthalate

Figure 4 shows the rate capabilities for dilithium terephthalate and **P1-Li**. For this test the current was increased from C/10 to C/2. It is evident, that the capacity decreases less severely for **P1-Li** than for dilithium terephthalate.

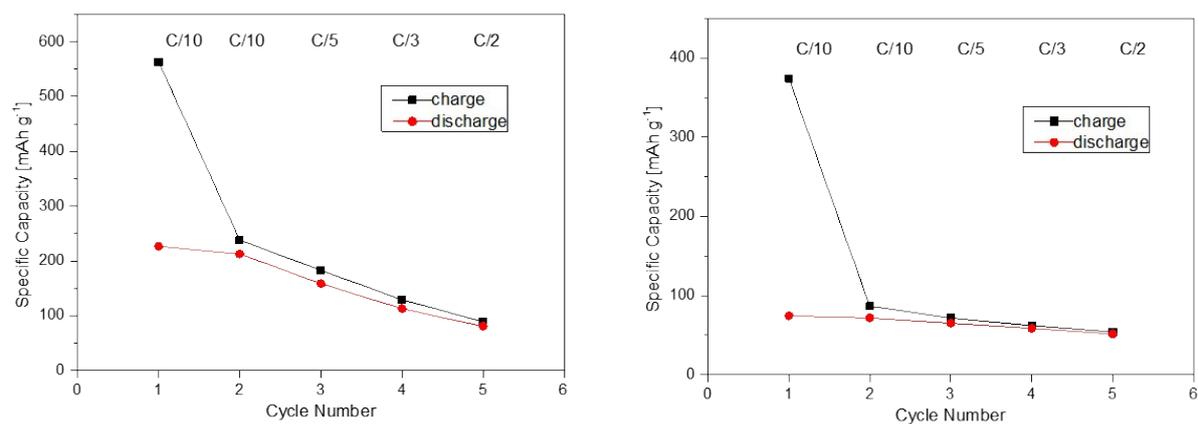


Figure 4: Comparison of rate capabilities of (left) dilithium terephthalate and (right) **P1-Li**. (See Figure 5 in the main manuscript for experimental details).

9. References

- ⁱ a) L. Anzalone, J. A. Hirsch, *J. Org. Chem.*, 1985, **50**, 2128.
- ⁱⁱ P.H. Nelson, K. G. Untch (Syntex Inc.), US3966820, **1976**.
- ⁱⁱⁱ a) X.-Y. Yin, C. Ye, X. Ma, E.-Q. Chen, X.-Y. Qi, X.-F. Duan, X.-H. Wan, S. Z. D. Cheng, Q.-F. Zhou, *J. Amer. Chem. Soc.*, 2003, **125**, 6854. b) D. Zhang, Y.-X. Liu, X.-H. Wan, Q.-F. Zhou, *Macromolecules* 1999, **32**, 5183. c) Y.-F. Zhao, Y. Yi, X. Fan, X. Chen, X. Wan, Q.-F. Zhou, *J. Polym. Sci. A*, 2005, **43**, 2666.
- ^{iv} M. Padmanaban, P. Müller, C. Lieder, K. Gedrich, R. Grünker, V. Bon, I. Senkovska, S. Baumgärtner, S. Opelt, S. Paasch, E. Brunner, F. Glorius, E. Klemm, S. Kaskel, *Chem. Commun.*, 2011, **47**, 12089.
- ^v K. Weinges, U. Reinel, W. Maurer, N. Gässler, *Liebigs Ann. Chem.*, 1987, 833.
- ^{vi} Y. Wu, H. Guo, X. Zhang, T. D. James, J. Zhao, *Chem. Eur. J.*, 2001, **17**, 7632.
- ^{vii} B. Häupler, R. Burges, C. Friebe, T. Janoschka, D. Schmidt, A. Wild, U. S. Schubert, *Macromol. Rapid Commun.* 2014, **35**, 1367.