SUPPLEMENTARY INFORMATION

Microwave-accelerated synthesis of lengthy and defect-free poly(*m*-phenyleneethynylene)s via AB' and A_2+BB' polycondensation routes

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General Methods

Synthesis. Compounds **A**,[1] **C**,[2] and monomer **1b**[2] were synthesized as described in the literature (SuppInfo: Figure 1). $Pd(PPh_3)_4$ was freshly prepared,[3] all other chemicals were commercial and used as received. Benzene and acetonitrile were distilled prior to use under N_2 atmosphere over sodium/benzophenone ketyl and calcium hydride, respectively. Microwave-assisted polycondensations were performed in a Thomtec (type MTW – O) microwave reactor, which monitors the sample temperature by IR and automatically adjusts the microwave power to maintain the programmed temperature. All the reactions were carried out at 60 % microwave power, i.e. 600 W. Column chromatography was carried out with 130-400 mesh silica gel.

Analytics. NMR spectra were recorded on Bruker AB 250 (250.1 and 62.9 MHz for ^1H and ^{13}C, respectively) and AC500 as well as Delta JEOL Eclipse 500 (500 and 126 MHz for ^1H and ^{13}C, respectively) spectrometers at 23 ± 2 ^oC using residual protonated solvent signal as internal standard (^1H: $\delta(CHCl_3)$ = 7.24 ppm, δ(DMSO) = 2.49, $\delta(CH_3CN)$ = 1.94 ppm and ^{13}C: $\delta(CHCl_3)$ = 77.0 ppm, δ(DMSO) = 39.7 ppm). Mass spectrometry was performed on Perkin-Elmer Varian Type MAT 771 and CH6 (EI) or Type CH5DF (FAB) instruments. UV/visible absorption spectra were recorded in spectroscopic grade chloroform and acetonitrile, respectively, using quartz cuvettes of 1 cm path length on a Cary 50 Spectrophotometer equipped with a Peltier thermostated cell holder (T = 25 ± 0.05 ^oC). IR spectra were recorded as KBr pellets on a Nicolet 5SXC FTIR-Interferometer. Elemental analyses were performed on a Perkin-Elmer EA 240. GPC measurements in THF as the mobile phase were performed on a Waters 515 HPLC pump-GPC system equipped with a Waters 2487 UV detector (254 nm detection wavelength) at 40 ^oC using a flow rate of 1 mL/min. The samples were separated through Waters Styragel HR1 or HR3

columns with 5 µm bead sizes, which were calibrated with several narrow polydispersity polystyrene samples using an internal toluene standard. GPC measurements in 0.5 wt % LiBr in NMP as the mobile phase were performed on a Thermo Separation Products SEC setup equipped with UV (TSP UV1000) and RI (Shodex RI-71) detectors at 70 ^{o}C using a flow rate of 1 mL/min. The column set employed was 300 x 0.8 cm, 10 μm PSS-GRAM: 30, 30, 100, 3000 Å. The columns were calibrated with several narrow polydispersity polystyrene samples. The HPLC system consisted of a Knaur Eurosphere 7µm C18, 4·120 mm silica gel column and UV-detection at 254 nm with an eluent flow of 1 mL/min.

Monomer synthesis

3,5-Diiodobenzoic acid (B):[4] Compound **A**[1] (1.6 g, 4 mmol) was dissolved in ethanol (5 mL) and 1 M aq. NaOH (20 mL), the solution was refluxed for 2 h at 70 °C, then allowed to cool to rt, and neutralized with 1 M HCl. The white precipitate that appeared immediately was filtered and washed with water followed by recrystallization from ethanol furnishing 1.3 g of the product as a white solid (87 % yield). Characterization data agreed with the literature.[4]

2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethyl 3,5-diiodobenzoate (2b): Compound **B** (4.7 g, 12mmol) was mixed with thionyl chloride (50 mL) and refluxed for 2 h. Excess thionyl chloride was removed *in vacuo* and the remaining residue was dried on a vacuum pump for 3 h to afford the crude acid chloride as a white solid. It was then added to a stirring solution of triethylene glycol monomethyl ether (1.88 mL, 12 mmol) and triethylamine (3.63 mL, 36 mmol) in 30 mL of CH_2Cl_2 at 0 °C. The suspension was allowed to warm to rt and stirred overnight. Then the organic layer was washed with brine and sat. aq. NH_4Cl solution. The residue was purified by column chromatography (50 % ethyl acetate in hexane) to yield 4.5 g of the product as a white solid (72 % yield). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.29(d, J = 1.8 Hz, 2 H, Ar-H), 8.20 (t, J = 1.8 Hz, 1 H, Ar-H), 4.44 (t, J = 5.1 Hz, 2 H, CO_2-CH_2), 3.79 (t, J = 5.1 Hz, 2 H, O-CH_2), 3.71-3.60 (m, 6 H, O-CH_2), 3.55-3.51 (m, 2 H, O-CH_2) 3.34 (s, 3 H, O-CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 163.54, 149.16, 137.68, 133.24, 94.27, 71.87, 70.59, 70.53, 68.92, 64.67, 58.95; FAB-MS (*m*-nitrobenzylalcohol (MNBA), 3 kV): *m/z* = 521.2 (calcd 521.1 for $C_{14}H_{19}O_5I_2^+$), 543.1 (calcd 543.0 for $C_{14}H_{18}O_5I_2Na^+$); Anal. C: 32.15, H: 3.13 (calcd C: 32.33, H: 3.49); HPLC (90 % MeOH / 10 % H_2O, 1 mL/min): 100.0 % peak area.

(2-Ethyl)-hexyl 3,5-diiodobenzoate (2a): Compound **B** (0.56 g, 1.5 mmol) was mixed with thionyl chloride (10 mL) and refluxed for 2 h. Excess thionyl chloride was removed *in vacuo* and the remaining residue was dried on a vacuum pump for 3 h to afford the crude acid chloride as a white solid. It was then added to a stirring solution of 2-ethyl-hexanol (0.19 mL, 1.5mmol) and triethylamine (0.62 mL, 4.5 mmol) in 10 mL of CH_2Cl_2 at 0 °C. The suspension was allowed to warm to rt and stirred overnight. Then the organic layer was washed with brine and sat. aq. NH_4Cl solution. The residue was purified by column chromatography (hexane) to yield 0.6 g of the product as colorless oil (82 % yield). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.26(d, J = 1.5 Hz, 1 H, Ar-H), 8.19 (t, J = 1.5 Hz, 2 H, Ar-H), 4.20 (d, J = 1.5 Hz, 2 H, CO_2-CH_2), 1.74-1.64 (m, 1 H, CH),1.46-1.22 (m, 8 H, CH), 0.94-0.88 (m, 6 H, CH); ^{13}C-NMR (125 MHz,$CDCl_3$): δ 163.73, 149.02, 137.61, 94.31, 68.18, 38.78, 30.43, 28.90, 23.86, 22.87, 13.98, 10.95; EI-MS (80 eV, 100 °C): *m/z* = 486.0 (calcd 486.1 for $C_{15}H_{20}O_2I_2^+$); HPLC (90% MeOH in H_2O, 1 mL/min): 99.37 % peak area.

(2-Ethyl)-hexyl 3-bromo-5-(3,3-diethyl-1-triazenyl)-benzoate (D): Compound **C** (1.64 g, 5 mmol), potassium carbonate (0.13 g, 1 mmol) and 2-ethyl-hexanol (2.3 mL, 15 mmol) were suspended in DMF (15 mL) and heated overnight at 140 °C. The reaction mixture was poured into water and extracted with hexane followed by column chromatography (2 % ethyl acetate in hexane) to give 1.8 g of product as yellow oil (87 % yield). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.94 (dd, J = 1.8 Hz, 1.8 Hz, 1 H, Ar-H), 7.84 (dd, J = 1.8 Hz, 1.8 Hz, 1 H, Ar-H), 7.71 (dd, J = 1.8, 1.8 Hz, 1 H, Ar-H), 4.15 (d, J = 5.4 Hz, 2H, CO_2-CH_2), 3.73 (q, J = 7.2 Hz, 4 H, NCH_2), 1.74-1.62 (m, 1 H, CH), 1.50-1.22 (m, 14 H, CH), 0.94-0.81 (m, 6 H, CH); ^{13}C- NMR (125 MHz, $CDCl_3$); δ 165.50, 152.61, 132.43,128.21, 126.84, 122.41, 120.86, 67.60, 38.88, 30.51, 28.92, 23.93, 22.87, 13.90, 10.95; FAB-MS (MNBA, 3 kV): *m/z* = 412.1 (calcd 412.1 for $C_{19}H_{30}N_3O_2Br^+$).

(2-Ethyl)-hexyl 3-(3,3-diethyl-1-triazenyl)-5-[2-(1,1,1-trimethylsilyl)-1-ethynyl]-benzoate (E): Dry and degassed triethylamine (50 mL) was added to a mixture of compound **D** (4.94 g, 12 mmol), $Pd(PPh_3)_4$ (0.27 g, 0.24 mmol), CuI (0.04 g, 0.24 mmol), and PPh_3 (0.31 g, 1.2 mmol) followed by the addition of trimethylsilylacetylene (3.4 mL, 24 mmol). The flask was sealed and the solution was stirred overnight at 80 °C. The reaction mixture was diluted with diethylether, filtered, and concentrated leaving a red colored oil, which was purified by column chromatography (2 % ethyl acetate in hexane) to give 4.12 g of the product as a yellow oil (80 %

yield). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.98 (dd, *J* = 2.2 Hz, 1.5 Hz, 1 H, Ar-H), 7.83 (dd, *J* = 2.2 Hz, 1.5 Hz, 1 H, Ar-H), 7.66 (dd, *J* = 2.2 Hz, 1.5 Hz, 1 H, Ar-H), 4.21 (d, *J* = 5.8 Hz, 2 H, CO_2-CH_2), 3.73 (q, *J* = 7.3 Hz, 4 H, NCH_2), 1.75-1.66 (m, 1 H, CH), 1.48-1.23 (m, 14 H, CH), 0.94-0.88 (m, 6 H, CH), 0.23 (m, 9H, $Si(CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$); δ 165.90, 151.27, 131.20, 128.97, 127.46, 123.65, 121.87, 104.42, 94.21, 67.29, 38.82, 30.47, 28.88, 23.87, 22.85, 13.92, 10.95, -0.20; EI-MS (80 eV, 120 °C): *m/z* = 429.4 (calcd 429.2 for $C_{24}H_{39}N_3O_2Si^+$); Anal. C: 67.21, H: 9.26, N: 9.14 (calcd C: 67.09, H: 9.15, N: 9.78).

(2-Ethyl)-hexyl 3-iodo-5-[2-(1,1,1-trimethylsilyl)-1-ethynyl]-benzoate (1a): Compound **E** (1.16 g, 2.7 mmol) was dissolved in 15 mL of CH_3I, the reaction mixture was degassed and refilled with argon three times then sealed and stirred at 110 °C for 16 h. The CH_3I was removed under reduced pressure and the brown colored residue was purified by column chromatography (2 % ethyl acetate in hexane) to give 0.85 g of the product as a light yellow oil (69 % yield). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.25 (dd, *J* = 1.5 Hz, 1.5 Hz, 1 H, Ar-H), 8.01 (dd, *J* = 1.5 Hz, 1.5 Hz, 1 H, Ar-H), 7.95 (dd, *J* = 1.5 Hz, 1.5 Hz, 1 H, Ar-H), 4.21 (d, *J* = 5.8 Hz, 2 H, CO_2-CH_2), 1.75-1.65 (m, 1 H, CH), 1.48-1.23 (m, 8 H, CH), 0.94-0.80 (m, 6 H, CH), 0.23 (s, 9 H, $Si(CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.45, 144.21, 138.11, 132.0, 125.3, 102.0, 97.07, 93.03, 67.99, 38.80, 30.45, 28.90, 23.88, 22.87, 13.94, 10.93, -0.30; EI-MS (80 eV, 90 °C): *m/z* = 456.3 (calcd 456.1 for $C_{20}H_{29}IO_2Si^+$), 441.2 (calcd 441.3 for $C_{19}H_{26}IO_2Si^+$); Anal. C: 52.0, H: 6.30 (calcd C: 52.64, H: 6.40); HPLC (95 % MeOH / 5 % H_2O, 1 mL/min): 95.0 % peak area.

Polymer synthesis

General procedure for AB´ polycondensation: The monomer (1 mmol), CuI (0.1 mmol) and the $Pd(PPh_3)_4$ (0.06 mmol) were loaded in a flame dried 10 mL Schlenk Tube, which was evacuated and refilled with argon. Dry and degassed benzene (for non-polar monomers **1a** and **2a**) or acetonitrile (for polar monomers **1b** and **2b**) (4 mL in each case) was submitted to the tube via a syringe, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 6 mmol) was added immediately followed by addition of distilled water (1-10 mmol depending on experiment, see manuscript: Table 1). The tube was covered with aluminum foil and the reaction mixture was allowed to stir at rt for 3 d. The reaction mixture was precipitated in 500 mL of methanol (for polymers **3a**) or diethyl ether (for polymers **3b**), the resulting solid was dissolved in CH_2Cl_2 and passed through a short silica column to give the desired polymer as light yellow colored solid.

General procedure for A_2+BB´ polycondensation: The monomer (1 mmol), CuI (0.1 mmol), and $Pd(PPh_3)_4$ (0.06 mmol) were loaded in a flame dried 10 mL Schlenk Tube, which was evacuated and refilled with argon. Dry and degassed benzene (for non-polar monomers **1a** and **2a**) or acetonitrile (for polar monomers **1b** and **2b**) (4.3 mL in each case) was submitted to the tube via a syringe, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 6 mmol) and trimethylsilylacetylene (TMSA, 1 mmol) were added immediately followed by addition of distilled water (1 mmol). The tube was covered with aluminum foil and the reaction mixture was allowed to stir at rt for 3 d. The reaction mixture was precipitated in 500 mL of methanol (for polymers **3a**) or diethyl ether (for polymers **3b**), the resulting solid was dissolved in CH_2Cl_2 and passed through a short silica column to give the desired polymer as light yellow colored solid.

Microwave-assisted polycondensation: The same procedures as described above were followed however, instead of stirring at rt the sealed tube was kept in the microwave reactor (for reaction times and temperatures see manuscript: Table 1).

***In-situ* ^{1}H-NMR experiment:** The AB' procedure was monitored by ^{1}H-NMR spectroscopy using CD_3CN as the solvent. After acquisition of the initial spectrum, DBU and water were added to initiate deprotection and hence polycondensation. After addition, ^{1}H-NMR spectra were taken at given time intervals, see SuppInfo: Figure 6. The deprotection can be followed by the TMS signal (shift indicates TMS-group transfer), while coupling can be monitored either in the aromatic or triglyme regions of the spectrum by the build-up of new peaks and increasing peak broadening caused by the formation of oligomers. Free terminal acetylene (expected at $\delta \sim 3.17$ ppm) cannot be detected since it would presumably be covered by the intense DBU signal.

Polymer characterization

Polymer 3a: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.16 (broad s, 2 H, Ar-H), 7.89 (broad s, 1 H, Ar-H), 4.27 (broad s, 2 H, CO_2-CH_2), 1.73 (broad s, 1 H, CH), 1.33 (broad s, 8 H, CH), 0.91 (broad s, 6 H, CH), see also SuppInfo: Figure 2a; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.17, 149.46, 138.04, 134.12, 94.71, 68.62, 39.22, 30.87, 29.34, 24.29, 23.28, 14.39, 11.34; for GPC, see manuscript: Table 1.; Anal. C: 74.26, H: 7.13 (calcd for $(C_{17}H_{20}O_2)_n$ C: 79.65, H: 7.86); IR (KBr): 3422, 2957, 2929, 2859, 1723, 1644, 1596, 1455, 1235, 1114 cm^{-1}, see also SuppInfo: Figure 3a; UV/vis ($CHCl_3$, 25 ^{o}C) λ_{max} = 290 nm, see also SuppInfo: Figure 4a.

Polymer 3b: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.20 (broad s, 2 H, Ar-H), 7.90 (broad s, 1 H, Ar-H), 4.52 (broad t, 2 H, CO_2-CH_2), 3.87 (broad t, 2 H, O-CH_2), 3.72 (broad m, 6 H, O-CH_2), 3.52 (broad t, 2 H, O-CH_2), 3.34 (broad s, 3 H, O-CH_3), see also SuppInfo: Figure 2b; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 165.05, 138.41, 132.91, 131.20, 123.70 89.12, 72.00, 70.76, 70.74, 70.69, 69.15, 64.66, 59.05, see also manuscript: Figure 1; for GPC, see manuscript: Table 1 and SuppInfo: Figure 5; Anal. C: 65.27, H: 5.62 (calcd for $(C_{16}H_{18}O_5)_n$ C: 66.19, H: 6.25); IR (KBr): 3435, 2873, 1724, 1597, 1451, 1243, 1110, 1029 cm^{-1}, see also SuppInfo: Figure 3b; UV/vis ($CHCl_3$, 25 ^{o}C) λ_{max} = 290, 304 (shoulder) nm, (CH_3CN, 25 ^{o}C) λ_{max} = 282 nm, see also SuppInfo: Figure 4b.

References

1 F. Li, S. I. Yang, Y. Ciringh, J. Seth, C. H. Martin, D. L. Singh, D. Kim, R. R. Birge, D. F. Bocian, D. Holten, and J. S. Lindsey, *J. Am. Chem. Soc*., 1998, **120**, 10001-10017.

2 J. Zhang, D. J. Pesak, J. L. Ludwick, and J. S. Moore, *J. Am. Chem. Soc*., 1994, **116**, 4227-4239.

3 D. R. Coulson, *Inorg. Syn.* **1971**, *13*, 121-4.

4 3,5-Diiodobenzoic acid has been described in the literature, for example: C. C. Mak, N. Bampos, S. L. Darling, M. Montalti, L. Prodi, J. K. M. Sanders, *J. Org. Chem.*, 2001, **66**, 4476-4486. However, we employed a different preparation procedure.

Figures

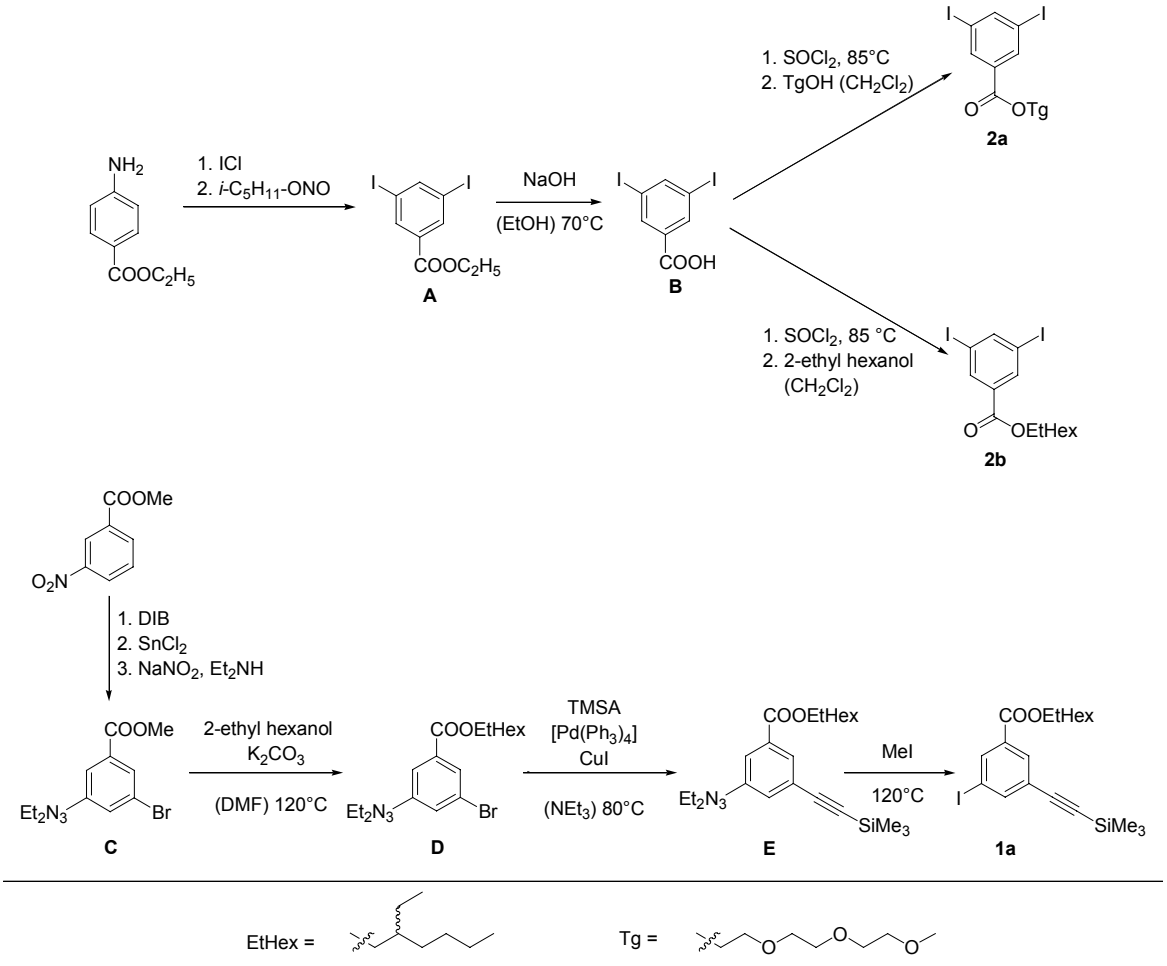

Figure 1. Monomer syntheses.

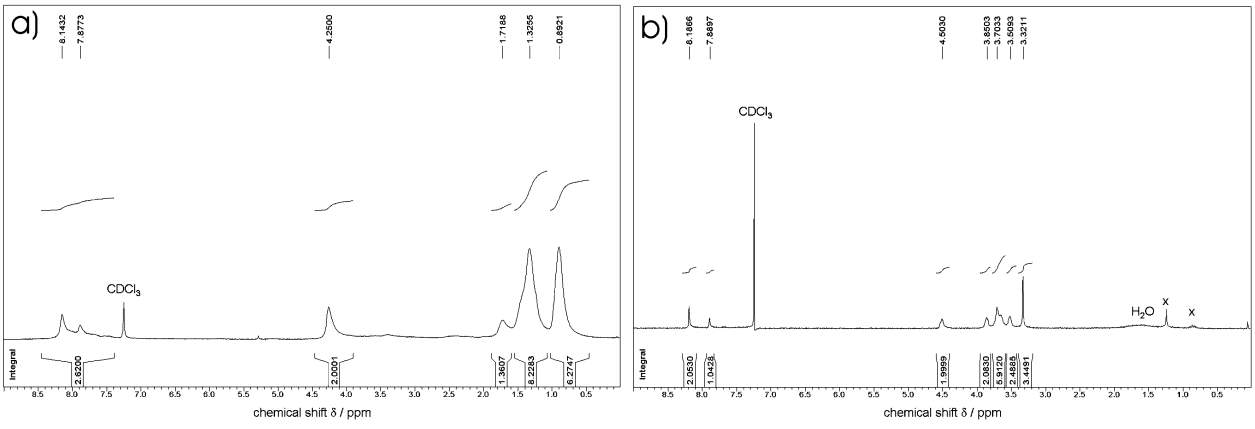

Figure 2. ^{1}H NMR spectra of: a) polymer **3a** and b) polymer **3b** (250 MHz, $CDCl_3$, 25 ^{o}C).

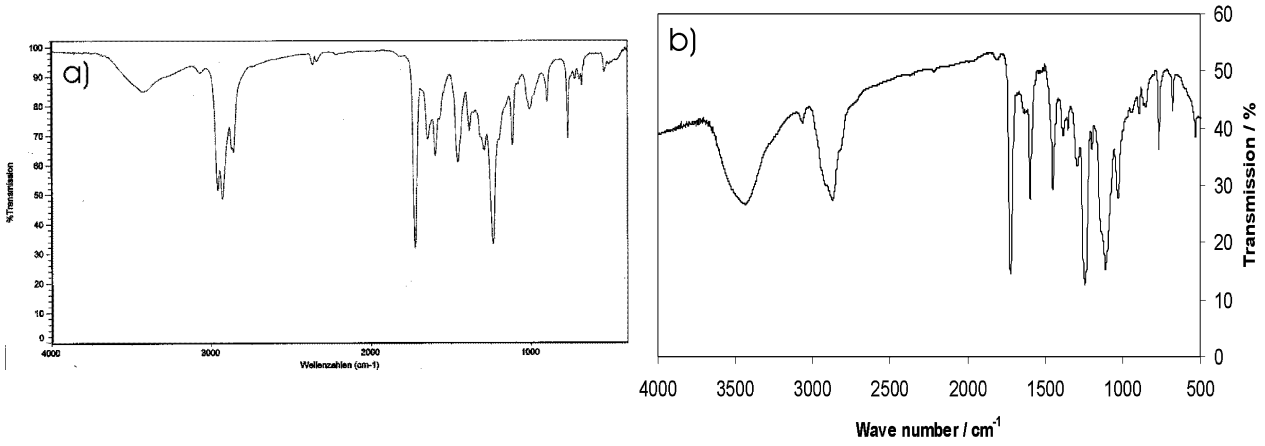

Figure 3. IR spectra of: a) polymer **3a** and b) polymer **3b** (KBr).

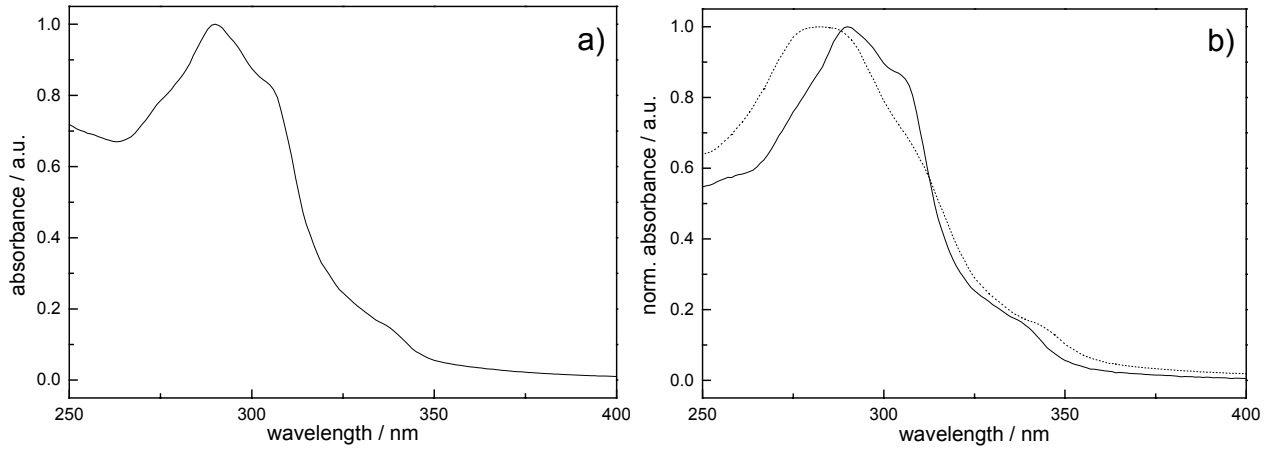

Figure 4. UV/vis absorption spectra of: a) polymer **3a** in $CHCl_3$ (——) and b) polymer **3b** in $CHCl_3$ (——) and CH_3CN (·····) (25 °C).

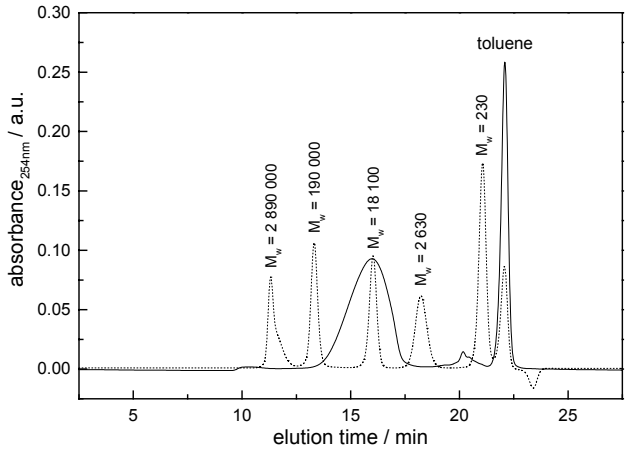

Figure 5. GPC trace of polymer **3b** made via the A_2+BB' polycondensation (manuscript: Table 1, entry 14). The polystyrene standards used for calibration and their respective molecular weights are shown (·····).

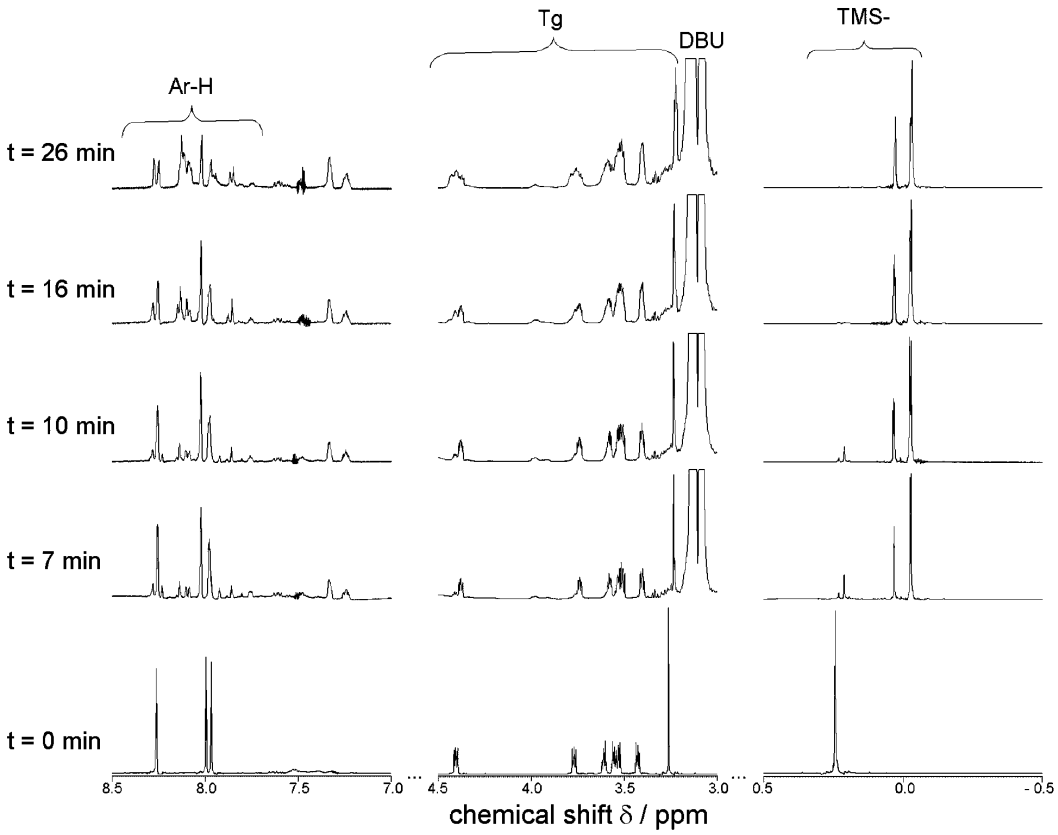

Figure 6. *In-situ* ^{1}H-NMR experiment following the AB' polycondensation of monomer **1b**. Representative regions diagnostic for aromatic, triglyme, and trimethylsilyl protons are shown at the given time intervals.