

## Chapter 3

### Synthesis of Poly(*ortho*-phenylene ethynylene)s

Synthesis of a poly(*ortho*-phenylene ethynylene) derivative has been achieved via our AB' polycondensation approach. Microwave irradiation is used to accelerate the polycondensation. The resulting polymer is characterized thoroughly by several analytical methods and optical spectroscopies.

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#### Introduction

Identification of new folding backbones and their synthesis present a challenging task. The main objective of this research is to create systems that mimic biomolecules, in order to understand sequence-structure and structure-property relationships. Synthesis and folding properties of *meta*-linked phenylene ethynylene oligomers have been studied thoroughly during the last decade.<sup>[1,2]</sup> However, their *ortho*-linked counterparts have received relatively little attention. Crystal structure data reported by Grubbs and Kratz<sup>[3]</sup> and theoretical study by Blatchly and Tew<sup>[4]</sup> have demonstrated the ability of these structures to adopt helical conformation. The helix in *ortho*-linked phenylene ethynylene structures is predicted to contain only three aromatic rings, i.e. 3<sub>12</sub>-helix (3 refers to number of repeat units per helical turn, while subscript 12 refers to bonds per turn). This results in a structure having practically no inner void and being more reminiscent of the 3<sub>10</sub> helix of the proteins.

Many research groups have synthesized well-defined *ortho*-linked phenylene ethynylene (*o*-PE) oligomers for different purposes. Nicoud and Wong<sup>[5]</sup> have synthesized donor-acceptor substituted trimer, tetramer, and a pentamer for studying non-linear optic properties. Anderson<sup>[6]</sup> has synthesized a series of phenylene ethynylene oligomers with different connectivities including an *ortho*-linked phenylene ethynylene pentamer for electroluminescence study. Tew and coworkers<sup>[7]</sup> have synthesized a series of non-polar *o*-PE up to the hexamer. Utilizing chiral

alkoxy-substituents, no helical conformation in solution could be detected by means of CD spectroscopy probably due to the short chain length and the destabilization effect of donor-substituents on  $\pi$ - $\pi$  stacking. The group of Bunz<sup>[8]</sup> has synthesized pyridine-capped *o*-PE for their use in light emitting diodes. All these groups utilize palladium-catalyzed coupling of an aryl halide to an aryl alkyne for synthesis of these oligomers. However, the group of Otera<sup>[9]</sup> has demonstrated a practically simple way of using a sulfone and an aldehyde, involving a one-pot procedure of subsequent aldol type addition, protection and elimination reactions. A series of *o*-PE oligomers have been synthesized using this protocol, the longest oligomer being the nonamer. Contrary to the oligomers, polymer synthesis has received very little attention. In fact, there are only two attempts to synthesize *o*-PE polymers. Shultz and Hollomon<sup>[10]</sup> have synthesized quinone-containing *o*-PEs with molecular weights of 9000-11000 corresponding to 22-25 repeat units. The group of Swager<sup>[11]</sup> synthesized exceptionally high molecular weight *o*-PE polymers ( $M_n = 260000$ ) employing excess of bisalkyne monomer.

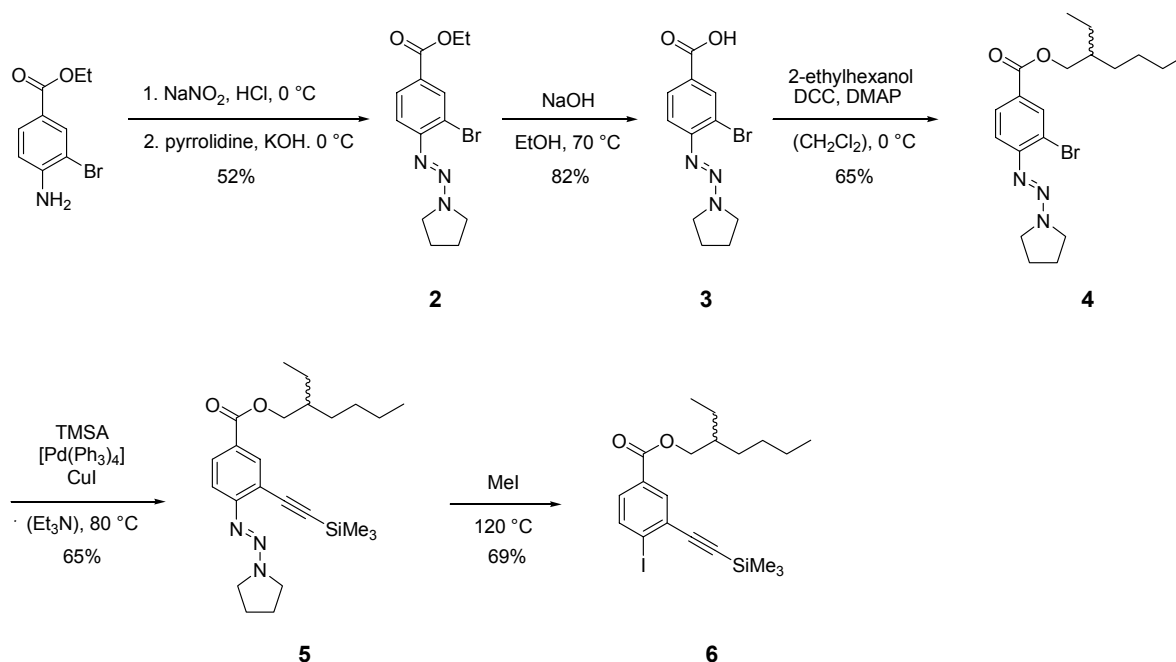
### Motivation

We aimed to extend our method of preparing defect free poly(*m*-phenylene ethynylene)s (Chapter 2) to synthesize *ortho*-linked poly(phenylene ethynylene)s. The folding properties of this backbone are still not explored and hence represent an attractive opportunity to study the secondary structure of this foldamer family.

### Monomer Synthesis

The AB' polycondensation route was chosen due to its advantage of using a stoichiometrically balanced monomer. The synthesis of monomer was accomplished in five steps linear sequence. The free amino group in ethyl 4-amino-3-bromobenzoate was converted to a triazene, which could be purified by crystallization. The ester **2** was saponified yielding acid **3** followed by esterification with 2-ethylhexanol. The branched alkyl side chain was chosen to impart good solubility to the growing polymer chain during polymerization and to render the resulting polymer soluble in different organic solvents for characterization. The bromide functionality was used to install the trimethylsilyl protected acetylene by palladium-catalyzed cross-coupling. The final step is the conversion of the triazene group to the iodide in boiling methyl iodide under inert atmosphere (Scheme 1).

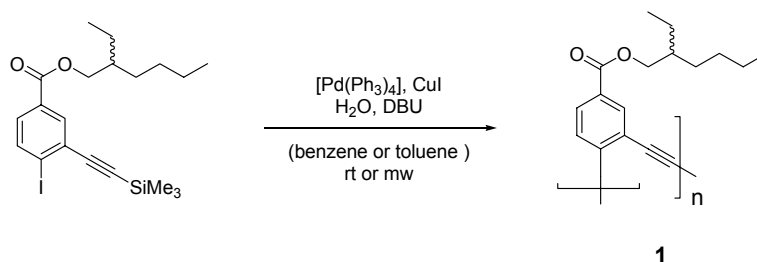
## Scheme 1



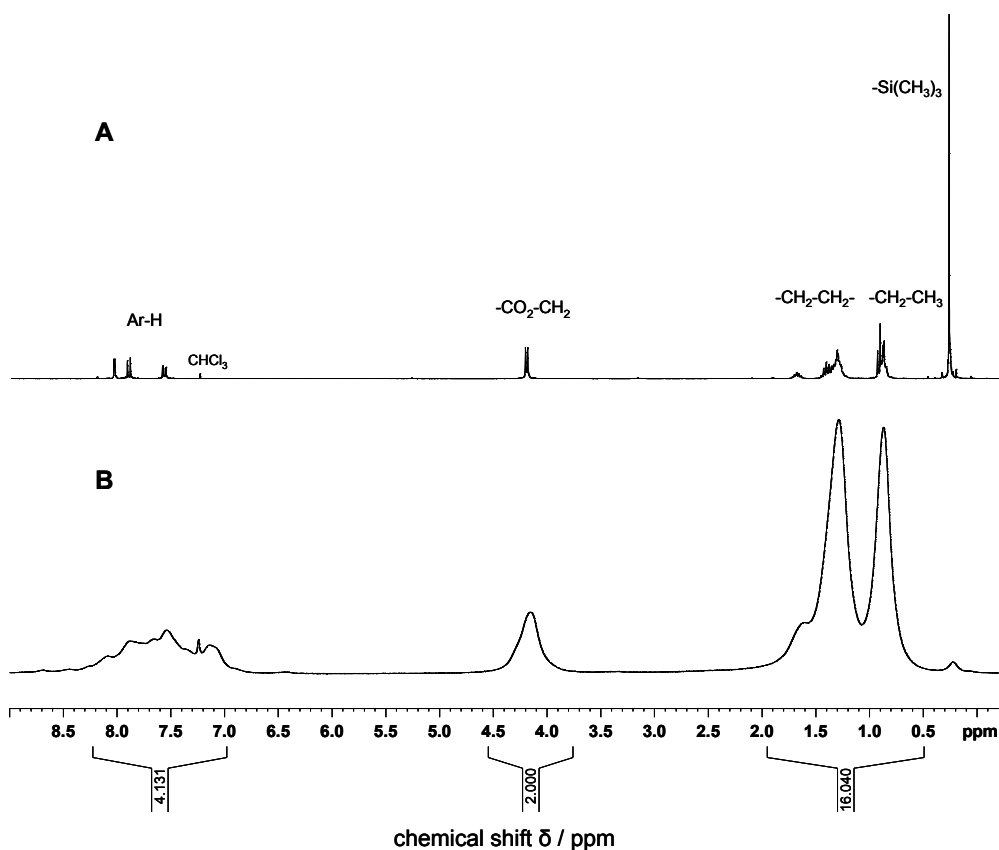
## Polymer Synthesis

The synthesis takes advantage of our *in-situ* activation/coupling protocol (Chapter 2) to synthesize poly(phenylene ethynylene)s (Scheme 2).

## Scheme 2



Initially, thermal reaction was carried out in benzene using 1 equivalent of water that resulted in very poor degree of polymerization (Table 1, entry 1). The solubility of the polymer was found to be increased in toluene, which was used as solvent for all later polycondensation reactions.



**Figure 1.**  $^1\text{H}$  NMR spectral comparison of monomer **6** (A) and polymer **1** (B) (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ).

The effect of water content on polycondensation is known from our previous work (Chapter 2), hence 10 equivalents of water were used. This resulted in polymers with higher molecular weight (Table 1, entry 3-5).

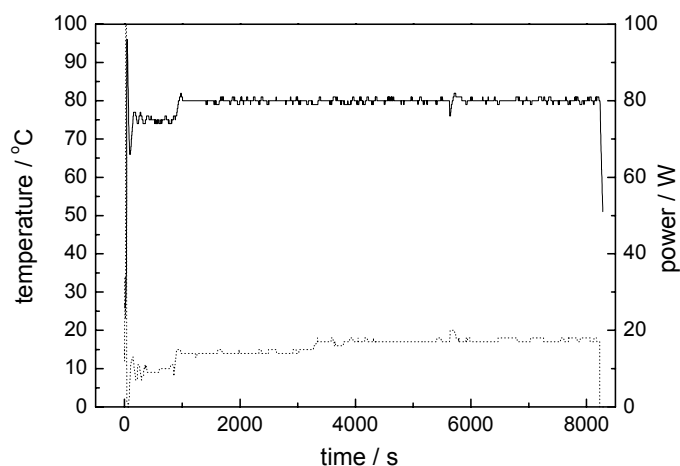
**Table 1** Selected polycondensation experiments according to the AB' approach illustrated in scheme 2.<sup>a</sup>

entry	solvent	$\text{H}_2\text{O}$ / equiv.	T / $^\circ\text{C}$	time / h	$M_w^b$	$M_n^b$	PDI <sup>b</sup>	DP ( $P_n$ ) <sup>b</sup>	Yield <sup>c</sup>
1	benzene	1	25	72	2800	2400	1.14	9	81
2	toluene	1	25	72	3600	3100	1.16	12	83
3	toluene	10	50 (mw <sup>d</sup> )	1	7800	6500	1.20	25	98
4	toluene	10	80 (mw <sup>d</sup> )	2.2	9600	7500	1.28	29	99
5	toluene	10	60	48	9200	7300	1.26	28	99

<sup>a</sup> conditions: 1 equiv. AB' monomer (**6**), 6 mol%  $\text{Pd}(\text{PPh}_3)_4$ , 6 mol%  $\text{CuI}$ , 6 equiv. DBU in 4 ml of solvent; <sup>b</sup> according to GPC in THF at 40  $^\circ\text{C}$ ; <sup>c</sup> isolated yield after precipitation in methanol; <sup>d</sup> microwave heating.

To shorten the reaction time, the effect of microwave irradiation was investigated. Two different polycondensation reactions varying both time and temperature were conducted. Both

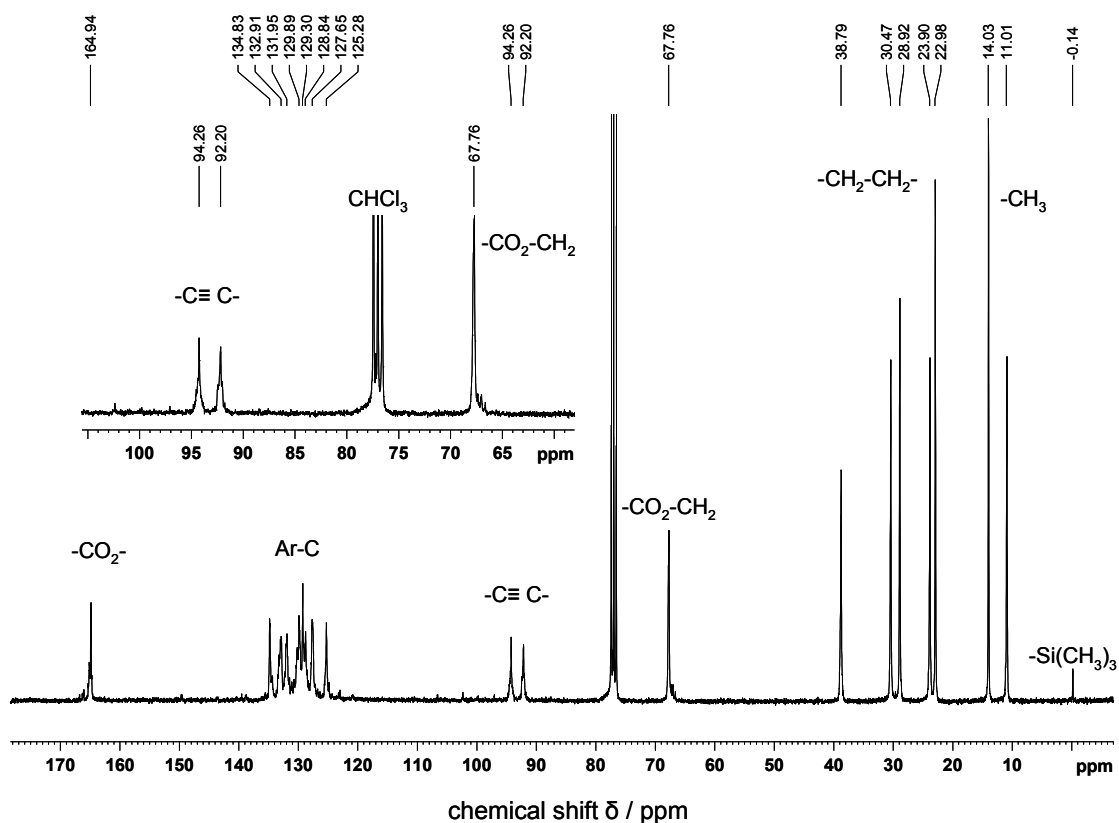
experiments gave similar results and the polycondensation time could be significantly reduced to 1 hour (Table 1, entry 3).



**Figure 2.** Microwave heating profile for polycondensation reaction (Table 1, entry 5) showing temperature (—) and microwave power (·····).

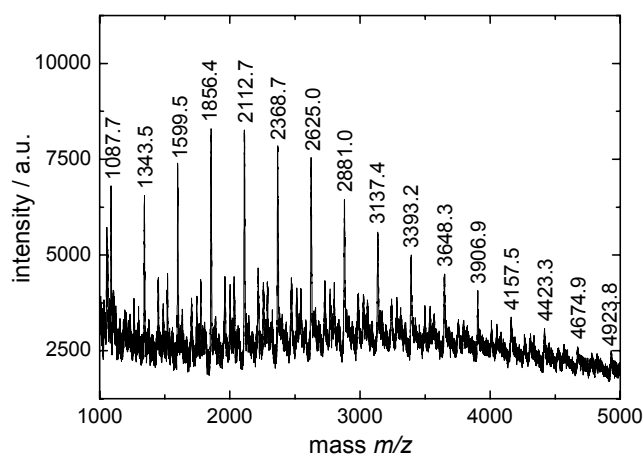
### Polymer Characterization

Polymers were obtained in almost quantitative yields after single precipitation into methanol. GPC analysis of polymer indicated reasonable degrees of polymerization and polydispersities typical for polycondensation processes (Table 1).  $^1\text{H-NMR}$  showed broad signals with no discernable end-groups (Figure 1). In  $^{13}\text{C-NMR}$  spectra no diacetylene defects could be detected even after a large numbers of scans (Figure 3).



**Figure 3.**  $^{13}\text{C}$  NMR spectrum of polymer 1 (300 MHz, 60000 Scans,  $\text{CDCl}_3$ , 25 °C). The inset shows the region of potential diacetylene defects.

The absence of diyne defects is very important as these defects are presumably detrimental to the formation of a stable secondary structure. MALDI-TOF mass spectrometry measurements confirmed the molecular weights detected by GPC (Table 1) and nicely shows the incorporation of the desired monomer units into the polymer backbone as indicated by the matching peak interval.

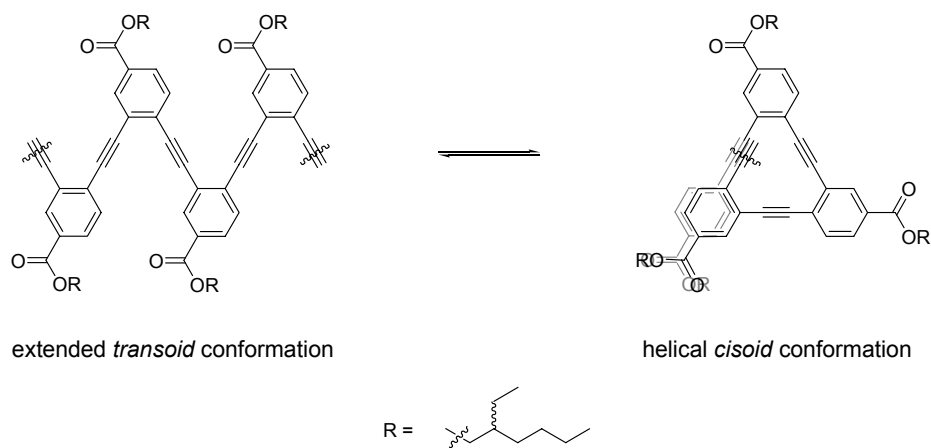


**Figure 4.** Maldi-TOF mass spectra of polymer **1**.

### Optical Properties

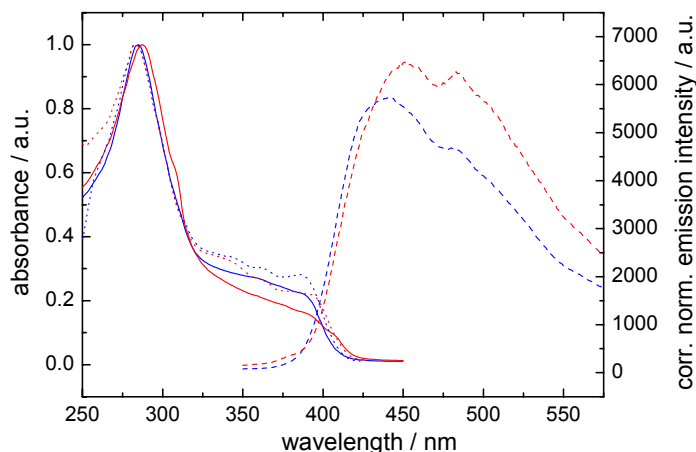
*Ortho*-linked phenylene ethynylene backbone can exist in two distinct conformations. The extended *transoid*-conformation and the helical *cisoid*-conformation (Scheme 3).

**Scheme 3**



We anticipated that the polymer **1**, appended with the non-polar side chains would undergo a solvophobic driven folding reaction. Solvents, such as chloroform, are expected to solvate both the backbone as well as the side chains thereby favoring an extended conformation, while non-polar solvents, such as cyclohexane should preferentially solvate the side chains causing the conformational transition from an extended to a helical structure.

In the extended conformation, the repeat units are planar and hence the extent of effective conjugation is expected to be large than in the helical conformation, where the non-planarity of the repeat units hampers  $\pi$ -electrons delocalization. This can be seen in the absorption spectra of the polymer **1** recorded in two different solvents (Figure 5). In chloroform, the absorption spectra exhibit a sharp band around 284 nm, intuitively assigned to the non-planar, isolated *ortho*-linked phenylene ethynylene chromophores and a broad band around 360 nm, attributed to the planar  $\pi$ -conjugated *ortho*-linked phenylene ethynylene repeat units. However, in the folding promoting solvent, i.e. cyclohexane, the intensity of the broad band indicative of the extended conformation diminishes suggesting increasing population of the helical conformation.



**Figure 5.** UV/vis absorption (—), emission (— —) and excitation (·····) spectra of polymer **1** in chloroform (blue) and cyclohexane (red) solution (25 °C).

Emission spectroscopy was used in order to get more insight into the conformational behavior of the polymer **1** (Figure 5). Two emission bands can be observed at 442 and 483 nm in chloroform, while at 452 and 483 nm in cyclohexane. The emission arising at 483 nm is indicative of stacked chromophores. As expected this band is more pronounced in the helix promoting solvent cyclohexane than in chloroform. These spectral differences in two different solvents point to the conformational transition of the polymer to a helical structure in non-polar solvents.

## Conclusion



A new poly(*ortho*-phenylene ethynylene) derivative has been synthesized via our *in-situ* activation/coupling protocol. The polycondensation reaction could be accelerated by use of microwave irradiation. The polymer is characterized by several analytical methods and is shown to have no structural defects. The optical spectra recorded in two different solvents point to different chain conformation depending on the nature of the solvent. A detailed analysis, involving discrete oligomers to elucidate the solution structure of this new foldamer backbone is currently ongoing.

## Experimental

**General Methods.** Compound **1**<sup>[12]</sup> was synthesized as described in the literature. Pd(PPh<sub>3</sub>)<sub>4</sub> was freshly prepared,<sup>[13]</sup> all other chemicals were commercial and used as received. Toluene was distilled prior to use under argon atmosphere over sodium and benzophenone. Column chromatography was carried out with 130-400 mesh silica gel. NMR spectra were recorded on Bruker AB 250 (250.1 and 62.9 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively), Bruker DPX 300 (300 and 75 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively), and AC 500 as well as Delta JEOL Eclipse 500 (500 and 126 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively) spectrometers at 23 ± 2 °C using residual protonated solvent signal as internal standard (<sup>1</sup>H: δ(CHCl<sub>3</sub>) = 7.24 ppm, δ(DMSO) = 2.49, δ(CH<sub>3</sub>CN) = 1.94 ppm and <sup>13</sup>C: δ(CHCl<sub>3</sub>) = 77.0 ppm, δ(DMSO) = 39.7 ppm). Mass spectrometry was performed on Perkin-Elmer Varian Type CH5DF (FAB) and CH6 (EI) instruments. Bruker Reflex with 337 nm laser excitation (MALDI-TOF) instruments. 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 were performed on an Agilent 1100 series HPLC system equipped with three 300 x 8 mm SDV columns (1,000,000 Å, 100,000 Å, 1000 Å) and one 50 x 8 mm SDV column (100 Å) using both UV (230 nm and 280 nm) and RI detection. The measurements were performed in THF at 30 °C using a flow rate of 1 mL/min. The columns were calibrated with several narrow polydispersity polystyrene samples. The HPLC system consisted of a Knauer Eurosphere 7µm C18, 4·120 mm silica gel column and UV-detection at 254 nm with an eluent flow of 1 mL/min.

**Optical spectroscopy.** UV/visible absorption and fluorescence emission/excitation spectra were recorded in various solvents of spectroscopic grade using quartz cuvettes of 1 cm path length on a Cary 50 Spectrophotometer and a Cary Eclipse Fluorescence Spectrophotometer, respectively, both equipped with Peltier thermostated cell holders (ΔT = ± 0.05 °C). Unless stated otherwise, all experiments were carried out at 25 ± 0.05 °C. The samples were excited at λ<sub>exc</sub> = 299 nm, slit widths were set to 10 nm bandpass for excitation and 10 nm bandpass for emission. Fluorescence spectra were corrected for variations in photomultiplier response over wavelength using correction curves generated on the instrument. The corrected fluorescence spectra were normalized by the exact optical density OD<sub>299nm</sub>. For UV-visible absorption OD(λ<sub>max</sub>) ~ 0.8 and for fluorescence measurements OD(λ<sub>max</sub>) ~ 0.09 were used.

**Microwave irradiation.** Microwave-assisted polycondensations were performed in a CEM-Discover mono-mode microwave reactor, having a continuous microwave power delivery system from 0-300 watts. The reactions were carried out in 10 mL sealed glass vials. The temperature was measured by an IR sensor on the outer surface of the reaction vessel.

### Monomer Synthesis

**3-bromo-4- (3,pyrrolidin -1-diazenyl)-ethylbenzoate (2):** 4-amino-3-bromo ethylbenzoate (8.7 g, 35.44 mmol) was dissolved in 7 mL of concentrated HCl at 0 °C and 25 mL of aqueous NaNO<sub>2</sub> (2.48 g, 36 mmol) solution was added dropwise. This solution was then poured at once into a stirring solution of 1M KOH (30 mL) and Pyrrolidine (6 mL) at 0 °C. The reaction mixture was stirred for 30 minutes during which orange colored solid appeared in the flask. The solid was filtered off and recrystallized from ethanol to give 6 g of product as red needles (52 % yield). <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ 8.22 (d, <sup>4</sup>J = 1.8 Hz, 1 H, Ar-H), 7.86 (dd, <sup>3</sup>J = 8.2, <sup>4</sup>J 1.8 = Hz, 1 H, Ar-H), 7.42 (d, <sup>3</sup>J = 8.2, 1 H, Ar-H), 4.32 (q, <sup>3</sup>J = 7.2 Hz, 2H, CO<sub>2</sub>-CH<sub>2</sub>), 3.94 (bt, <sup>3</sup>J = 6.3 Hz, 2 H, N-CH<sub>2</sub>), 3.72 (bt, <sup>3</sup>J = 6.3 Hz, 2 H, N-CH<sub>2</sub>), 2.08-2.00 (m, 4 H, CH-CH<sub>2</sub>), 1.36 (t, <sup>3</sup>J = 7.2 Hz, 3 H, C-CH<sub>3</sub>); <sup>13</sup>C- NMR (125 MHz, CDCl<sub>3</sub>): δ 165.52, 152.12, 134.56, 129.13, 118.99, 117.73, 60.94, 51.38, 47.18, 23.93, 23.45, 14.31; FAB-MS (MNBA, 3 kV): *m/z* = 325.8 (calcd 326.0 for C<sub>13</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>Br<sup>+</sup>), 347.7 (calcd for C<sub>13</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>BrNa<sup>+</sup>), Anal. C: 48.37, H: 4.94, N: 12.35 (calcd C: 47.87, H: 4.94, N: 12.88).

**3-bromo-4- (3,pyrrolidin -1-diazenyl)-benzoic acid (3):** Ester **2** (4.0 g, 12.2 mmol) was dissolved in a mixture of ethanol (16 mL) and 1M NaOH (50 mL) and refluxed at 100 °C for 2 hours. The resulting solution was then neutralized with 1M HCl and immediately filtered. The resulting white solid was washed with plenty of water to give 3 g of product as light yellow solid (82 % yield). <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ 8.22 (d, <sup>4</sup>J = 1.8 Hz, 1 H, Ar-H), 7.86 (dd, <sup>3</sup>J = 8.2, <sup>4</sup>J 1.8 Hz, 1 H, Ar-H), 7.42 (d, <sup>3</sup>J = 8.2, 1 H, Ar-H), 3.94 (bt, <sup>3</sup>J = 6.3 Hz, 2 H, N-CH<sub>2</sub>), 3.72 (bt, <sup>3</sup>J = 6.3 Hz, 2 H, N-CH<sub>2</sub>), 3.33 (bs, 1 H, COOH), 2.08-2.00 (m, 4 H, CH-CH<sub>2</sub>); <sup>13</sup>C- NMR (125 MHz, CDCl<sub>3</sub>): δ 165.54, 134.04, 129.28, 117.77, 47.36, 23.47; FAB-MS (MNBA, 3 kV): *m/z* = 297.7 (calcd 298.0 for C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>Br<sup>+</sup>). Anal. C: 45.98, H: 4.10, N: 12.83 (calcd C: 44.31, H: 4.06, N: 14.09).

### (2-ethyl)-hexyl 3-bromo-4- (3,pyrrolidin -1-diazenyl)-benzoate (4):

2-ethylhexanol (1.64mL, 10.5mmol) and (0.26g, 2.1 mmol) dimethylaminopyridine (DMAP) were added to a stirring solution of Acid **3** (3.1 g, 10.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> at 0°C. Then (2.17g,

10.5 mmol) dicyclohexylcarbodiimide (DCC) was added in two portions. The suspension was stirred at room temperature over night. The resulting brown suspension was filtered and washed with cold hexane followed by column chromatography (2 % ethyl acetate in hexane) to give 2.8 g of product as yellow oil (65 % yield). <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ 8.22 (d, <sup>4</sup>J = 1.8 Hz, 1 H, Ar-H), 7.86 (dd, <sup>3</sup>J = 8.2, <sup>4</sup>J = 1.8 Hz, 1 H, Ar-H), 7.42 (d, <sup>3</sup>J = 8.2, 1 H, Ar-H), 4.32 (q, <sup>3</sup>J = 7.2 Hz, 2H, CO<sub>2</sub>-CH<sub>2</sub>), 3.94 (bt, <sup>3</sup>J = 6.3 Hz, 2 H, N-CH<sub>2</sub>), 3.72 (bt, <sup>3</sup>J = 6.3 Hz, 2 H, N-CH<sub>2</sub>), 2.08-2.00 (m, 4 H, CH-CH<sub>2</sub>), 1.74-1.62 (m, 1 H, C-CH), 1.47-1.22 (m, 8 H, C-CH), 0.93-0.84 (m, 6 H, C-CH); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ 165.54, 152.05, 134.42, 128.99, 127.48, 118.98, 117.67, 67.35, 51.28, 47.11, 38.86, 30.51, 28.90, 23.93, 23.35, 22.87, 13.92, 10.97; FAB-MS (MNBA, 3 kV): *m/z* = 409.3 (calcd 409.1 for C<sub>19</sub>H<sub>28</sub>N<sub>3</sub>O<sub>2</sub>Br<sup>+</sup>), 431.0 (calcd 432.1 for C<sub>19</sub>H<sub>28</sub>N<sub>3</sub>O<sub>2</sub>BrNa<sup>+</sup>).

**(2-ethyl)-hexyl 4-(3-pyrrolidin-1-diazenyl)-3-[2-(1,1,1-trimethylsilyl)-1-ethynyl]-benzoate (5):** Dry and degassed triethylamine (50 mL) was added to a mixture of compound **4** (4.51 g, 11 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.25 g, 0.22 mmol), CuI (0.04 g, 0.24 mmol), and PPh<sub>3</sub> (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 behind a red colored oil, which was purified by column chromatography (2 % ethyl acetate in hexane) to give 3.06 g of the product as a yellow oil (65 % yield). <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ 8.22 (d, <sup>4</sup>J = 1.8 Hz, 1 H, Ar-H), 7.86 (dd, <sup>3</sup>J = 8.2, <sup>4</sup>J = 1.8 Hz, 1 H, Ar-H), 7.42 (d, <sup>3</sup>J = 8.2, 1 H, Ar-H), 4.32 (q, <sup>3</sup>J = 7.2 Hz, 2H, CO<sub>2</sub>-CH<sub>2</sub>), 3.94 (bt, <sup>3</sup>J = 6.3 Hz, 2 H, N-CH<sub>2</sub>), 3.72 (bt, <sup>3</sup>J = 6.3 Hz, 2 H, N-CH<sub>2</sub>), 2.08-2.00 (m, 4 H, CH-CH<sub>2</sub>), 1.74-1.62 (m, 1 H, C-CH), 1.47-1.22 (m, 8 H, C-CH), 0.93-0.84 (m, 6 H, C-CH), 0.23 (s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 166.10, 156.06, 134.93, 130.21, 126.35, 116.51, 102.54, 98.83, 67.31, 51.18, 46.85, 38.94, 30.57, 28.98, 23.97, 22.90, 13.96, 11.01, 0.40; FAB-MS (MNBA, 3 kV): *m/z* = 427.4 (calcd 427.2 for C<sub>24</sub>H<sub>37</sub>N<sub>3</sub>O<sub>2</sub>Si<sup>+</sup>), 450.0 (calcd 450.2 for C<sub>24</sub>H<sub>37</sub>N<sub>3</sub>O<sub>2</sub>Si Na<sup>+</sup>).

**(2-ethyl)-hexyl 4-iodo-3-[2-(1,1,1-trimethylsilyl)-1-ethynyl]-benzoate (6):** Compound **5** (1.16 g, 2.7 mmol) was dissolved in 25 mL of CH<sub>3</sub>I, the reaction mixture was degassed and refilled with argon three times then sealed and stirred at 110 °C for 18 h. The CH<sub>3</sub>I 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 light yellow oil (69 % yield). <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ 8.03 (d, <sup>4</sup>J = 1.8 Hz, 1 H, Ar-H), 7.92 (d, <sup>3</sup>J = 8.2, 1 H, Ar-H), 7.57 (dd, <sup>3</sup>J

= 8.2,  $^4J = 1.8$  Hz, 1 H, Ar-H), 4.20 (d,  $J = 5.8$  Hz, 2 H, CO<sub>2</sub>-CH<sub>2</sub>), 1.74-1.62 (m, 1 H, C-CH), 1.47-1.23 (m, 8 H, C-CH), 0.94-0.80 (m, 6 H, C-CH), 0.27 (s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 165.42, 140.32, 138.89, 133.16, 129.73, 128.76, 105.58, 99.86, 67.70, 38.76, 30.45, 28.88, 23.87, 22.87, 13.96, 10.99, -0.32; EI-MS (80 eV, 90 °C):  $m/z = 455.9$  (calcd 456.1 for C<sub>20</sub>H<sub>29</sub>IO<sub>2</sub>Si<sup>+</sup>), Anal. C: 52.0, H: 6.30 (calcd C: 52.63, H: 6.40); HPLC (95 % MeOH / 5 % H<sub>2</sub>O, 1 mL/min): 97.0 % peak area.

### Polymer synthesis

**General procedure for polycondensation:** The monomer **6** (1 mmol), CuI (0.1 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.06 mmol) were loaded in a flame dried 10 mL Schlenk Tube, which was evacuated and refilled with argon. Dry and degassed benzene or toluene (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 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 and filtered to give desired polymer as grey colored solid.

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

### Polymer characterization

**Polymer 1:** <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ 7.65 (broad s, 3 H, Ar-H), 4.14 (broad s, 2 H, CO<sub>2</sub>-CH<sub>2</sub>), 1.63 (broad s, 3 H, C-CH), 1.27 (broad s, 6 H, C-CH), 0.86 (broad s, 6 H, C-CH), <sup>13</sup>C-NMR (500 MHz, CDCl<sub>3</sub>): δ 165.15, 134.85, 132.89, 131.92, 130.21, 129.28, 128.80, 127.69, 125.29, 94.25, 92.18, 67.73, 38.76, 30.44, 28.92, 23.85, 22.94, 14.00, 10.90; for GPC, see Table 1; Anal.C: 70.43, H: 7.08 (calcd for (C<sub>17</sub>H<sub>20</sub>O<sub>2</sub>)<sub>n</sub> C: 79.65, H: 7.86); IR (KBr): 3434, 2959, 2928, 2859, 1719, 1599, 1459, 1276, 1232, 1119, 763 cm<sup>-1</sup>; UV/vis (CHCl<sub>3</sub>, 25 °C) λ<sub>max</sub> = 284 nm.

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