

# Poly(*ortho*-phenylene ethynylene)s: Synthetic Accessibility and Optical Properties

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**ABSTRACT:** Poly(*ortho*-phenylene ethynylene)s (PoPEs) have been synthesized via an *in situ* activation/coupling AB' polycondensation protocol. The resulting polymers have been characterized by several analytical methods and are shown to have no structural defects. Although the Sonogashira–Hagihara polycondensation reaction is less efficient than for the preparation of the corresponding meta- and para-linked polymers, presumably because of steric hindrance caused by the *ortho* substituents, the process can be accelerated by the use of microwave irradiation. Optical spectroscopy indicates solvent-dependent conformational changes between extended transoid and helical cisoid conformations, providing the first experimental evidence for solvophobicity driven folding of the PoPE backbone. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 1619–1627, 2006

**Keywords:** conformational analysis; conjugated polymers; foldamers; microwave acceleration; poly(*ortho*-phenylene ethynylene); polycondensation

## INTRODUCTION

The identification and synthesis of new folding backbones is of particular importance for using foldamers<sup>1</sup> as conformationally defined macromolecular components in future smart materials.<sup>2,3</sup> In this context, the folding properties of amphiphilic meta-linked phenylene ethynylene oligomers have been studied extensively during the past decade.<sup>4–6</sup> However, their *ortho*-linked counterparts have received relatively little attention. Crystal structure data<sup>7</sup> and a theoretical study<sup>8</sup> have suggested the ability of these structures to adopt stable helical conformations. The helix in *ortho*-linked phenylene ethynylene structures is predicted to contain only three aromatic rings and is therefore classified as  $3_{12}$ -helix (3 refers to the number of repeat units per helical turn,

whereas the subscript 12 refers to the number of bonds per turn). This results in a structure having practically no inner void and being more reminiscent of the  $3_{10}$ -helix, which is highly abundant in proteins.

Series of well-defined and sequence-specific oligo(*ortho*-phenylene ethynylene)s<sup>9–14</sup> and *ortho*-phenylene ethynylene macrocycles<sup>15</sup> have been synthesized by several research groups for investigating their optical, electronic, and structural properties. Contrary to these studies involving oligomers, the synthesis of the corresponding polymers has received very little attention. The low-yielding Sonogashira–Hagihara reaction involving the *ortho* substituents limits the synthesis of high-molecular-weight poly(*ortho*-phenylene ethynylene)s (PoPEs) via polycondensation routes in accordance with the Carothers equation.<sup>16–19</sup> In fact, there have been only two reported attempts to synthesize PoPEs. Shultz and Hollomon<sup>20</sup> synthesized quinone-containing PoPEs with number-average molecular weights of 9000–11,000 corresponding to degrees of polymerization

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of 22–25. The group of Swager<sup>21</sup> prepared an exceptionally high-molecular-weight PoPE (number-average molecular weight = 260,000) by employing their standard method involving the use of a slight excess of a bisalkyne monomer to compensate for diyne defect formation. However, in both cases, the solution conformation was not investigated.

We recently reported the synthesis of lengthy and defect-free poly(*meta*-phenylene ethynylene)s by an *in situ* activation/coupling polycondensation protocol.<sup>22</sup> Encouraged by these results, we aimed to extend our method to prepare synthetically more difficult ortho-linked poly(phenylene ethynylene)s (PPEs). Because helical folding of this backbone class could thus far not be established experimentally,<sup>11,23</sup> the polymers prepared in the context of this study represent an attractive opportunity to investigate the secondary structure of this particular foldamer family.

## EXPERIMENTAL

### General Methods and Materials

Ethyl 4-amino-3-bromobenzoate (**1**) was synthesized as described in the literature.<sup>24</sup> Pd(PPh<sub>3</sub>)<sub>4</sub> was freshly prepared;<sup>25</sup> all other chemicals were commercial and were used as received. Toluene was distilled before use under an argon atmosphere over sodium and benzophenone. Microwave-assisted polycondensations were performed in a CEM-Discover monomode microwave reactor having a continuous microwave power delivery system from 0 to 300 W. The reactions were carried out in 10-mL sealed glass vials. The temperature was monitored by an IR sensor on the outer surface of the reaction vessel. 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), AC 500, and Delta JEOL Eclipse 500 (500 and 126 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively) spectrometers at 23 ± 2 °C with residual protonated solvent signals as the 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; <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 CH5DF (fast atom bombardment) and CH6 (electron impact) instruments. Matrix-assisted laser desorption/ionization time-of-flight

(MALDI-TOF) mass spectrometry was performed on an Applied Biosystems instrument (337-nm laser excitation) with dihydrobenzoic acid as a matrix. IR spectra were recorded as KBr pellets on a Nicolet 5SXC Fourier transform infrared interferometer. Elemental analyses were performed on a PerkinElmer EA 240. Gel permeation chromatography (GPC) measurements were performed on an Agilent 1100 series high-performance liquid chromatography (HPLC) system equipped with three 300 × 8 mm SDV columns (1,000,000, 100,000, and 1000 Å) and one 50 × 8 mm SDV column (100 Å) with both UV (230 and 280 nm) and refractive-index detection. The measurements were performed in tetrahydrofuran (THF) at 30 °C at 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 7-μm C18, 120-mm silica gel column and UV detection at 254 nm with an eluent flow of 1 mL/min.

### Optical Spectroscopy

Ultraviolet–visible (UV–vis) absorption and fluorescence emission/excitation spectra were recorded in various solvents of spectroscopic grade with quartz cuvettes of a 1-cm path length on a Cary 50 spectrophotometer and a Cary Eclipse fluorescence spectrophotometer, respectively, both equipped with Peltier thermostated cell holders (Δ*T* = ±0.05 °C). Unless stated otherwise, all experiments were carried out at 25 ± 0.05 °C. The samples were excited at an excitation wavelength of 285 nm, and slit widths were set to a 10-nm bandpass for excitation and a 10-nm bandpass for emission. Fluorescence spectra were corrected for variations in the photomultiplier response over the wavelength with correction curves generated on the instrument. The corrected fluorescence spectra were normalized by the exact optical density at 285 nm. For UV–vis absorption, the optical density at the maximum wavelength was approximately 1, and for fluorescence measurements, an optical density at the maximum wavelength of approximately 0.09 was used.

### Synthesis

#### *Ethyl 3-Bromo-4-(3'-pyrrolidin-1'-diazenyl)-benzoate (2)*

**1** (8.7 g, 35.4 mmol) was dissolved in 10 mL of concentrated HCl at 0 °C, and 25 mL of an aque-

ous NaNO<sub>2</sub> (2.48 g, 36 mmol) solution was added dropwise. After the complete addition of NaNO<sub>2</sub>, the reaction mixture was poured at once into a stirring solution of 1 M aqueous KOH (30 mL) and pyrrolidine (6 mL) at 0 °C. The reaction mixture was stirred for 30 min, during which time an orange solid appeared in the flask. The solid was filtered off and recrystallized from ethanol to give 6 g of the 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, 2 H, 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. Fast atom bombardment mass spectrometry [FABMS; MNBA (meta-Nitrobenzoic Acid), 3 kV]: *m/z* = 325.8 (calcd. 326.1 for C<sub>13</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>Br<sup>+</sup>). ELEM. ANAL. Found: 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 16 mL of ethanol and a 1 M NaOH (50 mL) solution. The reaction mixture was then refluxed at 100 °C for 2 h. The resulting solution was neutralized with 1 M HCl and immediately filtered. The resulting white solid was washed with plenty of water to give 3 g of the product as a 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. FABMS (MNBA, 3 kV): *m/z* = 297.7 (calcd. 298.1 for C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>Br<sup>+</sup>). ELEM. ANAL. Found: C, 45.98%; H, 4.10%; N, 12.83% (calcd.: C, 44.31%; H, 4.06%; N, 14.09%).

### (2-Ethyl)-1-hexyl 3-Bromo-4-(3'-pyrrolidin-1'-diazenyl)-benzoate (4)

2-Ethylhexanol (1.64 mL, 10.5 mmol) and dimethylaminopyridine (DMAP; 0.26 g, 2.1 mmol) were added to a stirring solution of acid **3** (3.1 g, 10.5 mmol) in 30 mL of CH<sub>2</sub>Cl<sub>2</sub> at 0 °C. Dicyclo-

hexyl carbodiimide (DCC; 2.17 g, 10.5 mmol) was added to the reaction mixture in two portions. The suspension was stirred at room temperature over night. The resulting brown suspension was filtered and washed with cold hexane, and this was followed by column chromatography (2% ethyl acetate in hexane) to give 2.8 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). <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. FABMS (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)-1-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 ester **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 diethyl ether, filtered, and concentrated, leaving behind a red oil, which was purified by column chromatography (2% ethyl acetate in hexane) to furnish 3 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. FABMS (MNBA, 3 kV): *m/z* = 427.4 (calcd. 427.6 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>SiNa<sup>+</sup>).

**Table 1.** Selected Polycondensation Experiments according to the AB' Approach Illustrated in Scheme 2<sup>a</sup>

Entry	Solvent	H <sub>2</sub> O (equiv)	Temperature (°C)	Time (h)	<i>M</i> <sub>w</sub> <sup>b</sup>	<i>M</i> <sub>n</sub> <sup>b</sup>	PDI <sup>b</sup>	DP <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	60	48	9200	7300	1.26	28	99
4	Toluene	10	80 (mw <sup>d</sup> )	2.2	9600	7500	1.28	29	99
5	Toluene	10	50 (mw <sup>d</sup> )	1	7800	6500	1.20	25	98

<sup>a</sup> Conditions: 1 equiv of the AB' monomer (**6**), 6 mol % Pd(PPh<sub>3</sub>)<sub>4</sub>, 6 mol % CuI, and 6 equiv of DBU in 4 mL of the solvent.

<sup>b</sup> Weight-average molecular weight (*M*<sub>w</sub>), number-average molecular weight (*M*<sub>n</sub>), polydispersity index (PDI), and degree of polymerization (DP) according to GPC in THF at 40 °C.

<sup>c</sup> Isolated yield after precipitation in methanol.

<sup>d</sup> Microwave heating.

### (2-Ethyl)-1-hexyl 4-iodo-3-[2'-(1,1,1-trimethylsilyl)-1'-ethynyl]-benzoate (**6**)

Ester **5** (1.16 g, 2.7 mmol) was dissolved in 25 mL of methyl iodide, and the reaction mixture was thoroughly degassed and refilled with argon three times and then sealed and stirred at 110 °C for 18 h. The excess of methyl iodide was removed under reduced pressure, and the brown 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).

<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, <sup>4</sup>*J* = 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. Electron-impact mass spectrometry (80 eV, 90 °C): *m/z* = 455.9 (calcd. 456.4 for C<sub>20</sub>H<sub>29</sub>IO<sub>2</sub>Si<sup>+</sup>). ELEM. ANAL. Found: 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.

### General Procedure for Polycondensation

Monomer **6** (1 mmol), CuI (0.1 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.06 mmol) were loaded into 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, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 6 mmol) was added and immediately followed by the addition of distilled water (1–10 mmol, depending on the experiment; see Table 1). The tube was covered with aluminum foil, and the reaction mixture

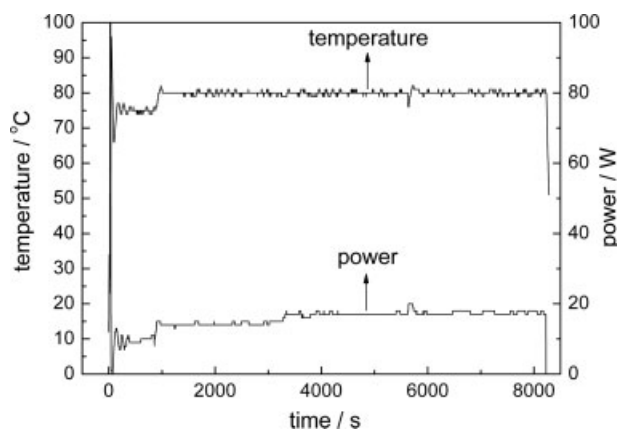
was allowed to stir at room temperature for 3 days. The reaction mixture was precipitated in 500 mL of methanol and filtered to give the desired polymers as gray solids.

### Microwave-Assisted Polycondensation

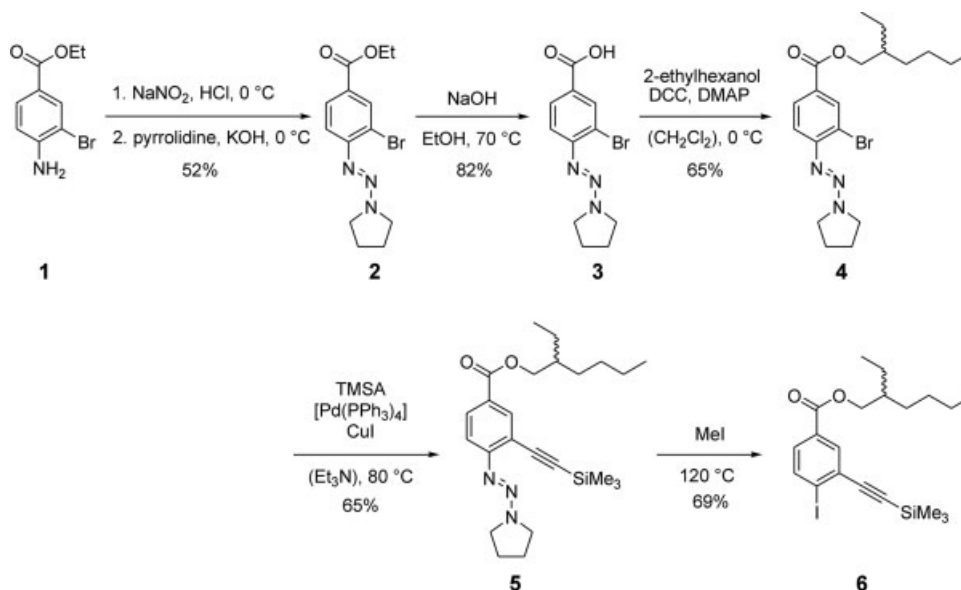
The same procedures described previously were followed; however, instead of stirring at room temperature, the sealed tube was kept in a microwave reactor (for the reaction times and temperatures, see Table 1 and Fig. 1).

### Polymer Characterization

<sup>1</sup>H NMR (300 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; see also Fig. 1). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δ): 165.15, 134.85, 132.89, 131.92, 130.21, 129.28, 128.80,



**Figure 1.** Microwave heating profile for the polycondensation reaction (Table 1, entry 4), showing the temperature and microwave power as functions of time.



Scheme 1

127.69, 125.29, 94.25, 92.18, 67.73, 38.76, 30.44, 28.92, 23.85, 22.94, 14.00, 10.90 [see also Fig. 3 (shown later); for GPC, see Table 1]. ELEM. ANAL. Found: C, 70.43%; H, 7.08 [calcd. for  $(C_{17}H_{20}O_2)_n$ : C, 79.65%; H, 7.86%]. IR (KBr): 3434, 2959, 2928, 2859, 1719, 1599, 1459, 1276, 1232, 1119, 763  $cm^{-1}$ . UV-vis ( $CHCl_3$ , 25 °C):  $\lambda_{max} = 284$  nm [see also Fig. 6 (shown later)].

## RESULTS AND DISCUSSION

### Monomer Synthesis

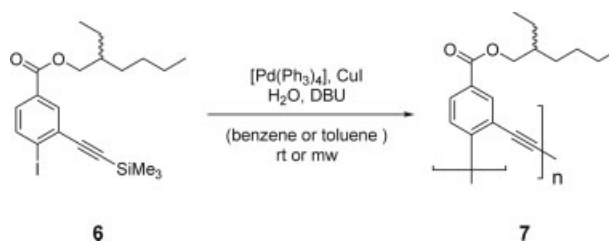
The synthesis of monomer **6** was accomplished in five linear synthetic steps. The starting material (**1**) is readily available by *ortho* monobromination of the activated ethyl 4-aminobenzoate.<sup>24</sup> Although the bromine substituent in **1** serves to introduce the acetylene moiety, the amino group is masked as a triazene, which can be converted to the desired iodine functionality. Triazene formation was readily accomplished, and cyclic pyrrolidine derivative **2** was chosen because its high crystallinity facilitated purification on a large scale. Saponification of the ester functionality yielded benzoic acid **3**, which was esterified with racemic 2-ethylhexanol to yield ester **4**. The branched alkyl side chain was deliberately chosen to impart good solubility to the growing polymer chain during polymerization<sup>17</sup> and to render the resulting polymer soluble in different organic solvents for further characterization.

With standard palladium-catalyzed cross-coupling methodology, aryl bromide **4** was converted to the corresponding trimethylsilyl-protected phenylacetylene **5**. Finally, aryl iodide **6** was formed by the reaction of triazene **5** with boiling methyl iodide under an inert atmosphere (Scheme 1).

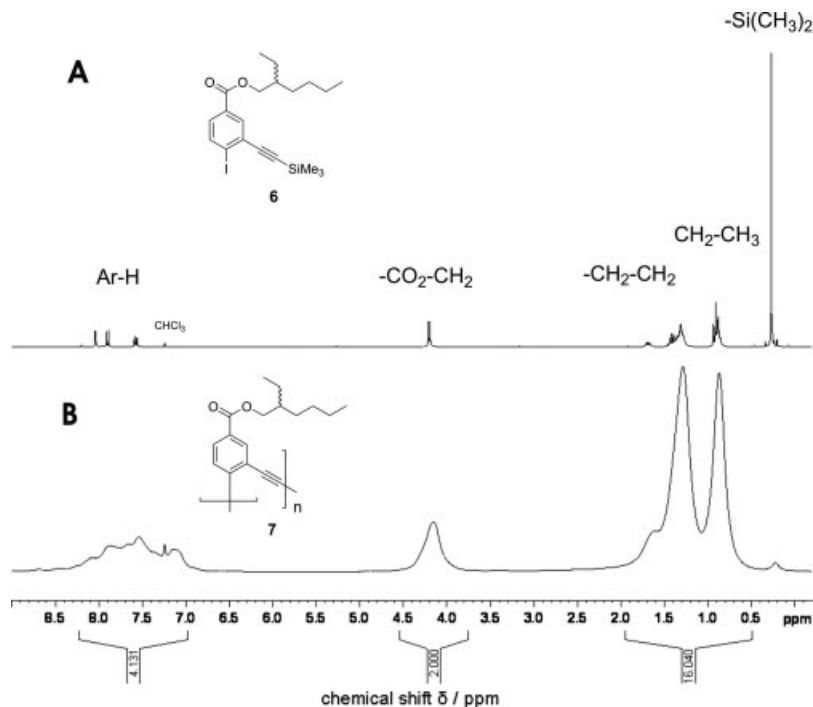
### Polymer Synthesis and Characterization

Polymer synthesis involves our one-pot activation/coupling AB' polycondensation protocol<sup>22</sup> to synthesize defect-free PPEs (Scheme 2). The rate-limiting *in situ* deprotection step minimizes the concentration of the free terminal acetylene in the reaction mixture and hence limits competing side reactions such as diyne defect formation. The absence of diyne defects is crucial as these defects are presumably detrimental to the formation of a stable secondary structure.

To optimize the polycondensation reaction, several parameters were varied. Initially, thermal reactions were carried out in benzene with 1 equiv of water, and this resulted in very low



Scheme 2



**Figure 2.**  $^1\text{H}$  NMR spectral comparison of (A) monomer **6** and (B) polymer **7** (300 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ).

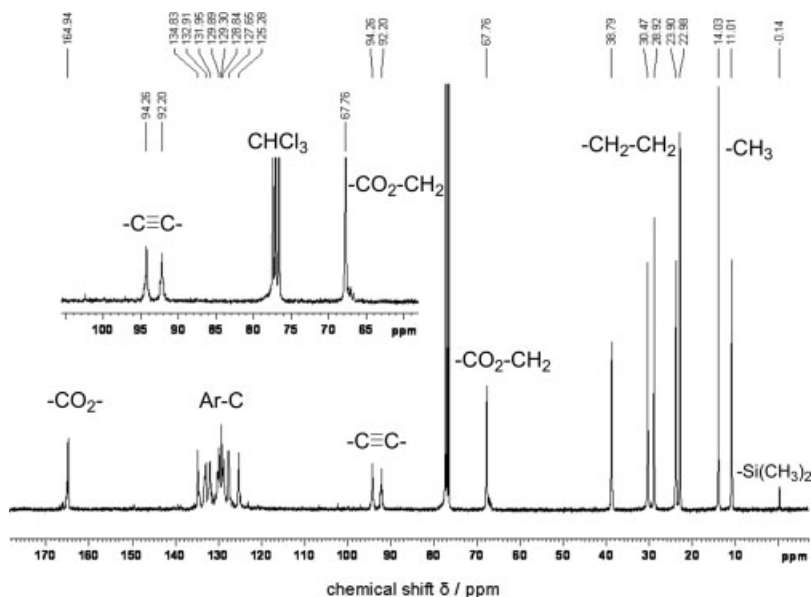
degrees of polymerization (Table 1, entry 1). The solubility of the polymer was increased in toluene, and hence toluene was used as a solvent for later polycondensation reactions, giving slightly better results (Table 1, entry 2). In a subsequent screening of the reaction conditions, the content of water was increased to 10 equiv, and the temperature was raised to  $60^\circ\text{C}$ . These new conditions furnished polymers of significantly higher molecular weight in less time and a practically quantitative yield (Table 1, entry 3). To further shorten the required reaction times, the effect of microwave irradiation<sup>26</sup> was investigated. Two different polycondensation reactions, with both the time and temperature varied, were performed (Table 1, entries 4 and 5). The two experiments gave similar results, and the polycondensation time could be significantly reduced from 2 days to 1 h (Table 1, entry 5).

The corresponding temperature and power profiles of a typical microwave-accelerated polycondensation experiment are shown in Figure 1. Polymers were obtained in almost quantitative yields after single precipitation into methanol. GPC analysis of the polymers showed monomodal distributions with reasonable degrees of polymerization and polydispersities typical for polycondensation processes (Table 1).<sup>27</sup>  $^1\text{H}$  NMR showed

broad signals with no discernable end groups (Fig. 2).

The obtained polymers were thoroughly analyzed by  $^{13}\text{C}$  NMR spectroscopy to detect potential diyne defects. Such defects should give rise to four individual signals in the region of  $77 \leq \delta \leq 82$  ppm, as evidenced by known spectral data of a structurally related macrocycle and oligomer.<sup>28</sup> However, no such signals were detected even after exhaustive scanning of concentrated samples of polymer **7**. Instead, two signals of the acetylene carbons of polymer **7** can clearly be seen at  $\delta = 92.2$  ppm and  $\delta = 94.3$  ppm (Fig. 3). The observation of two different signals for the ethynylene unit is due to the absence of molecular symmetry arising from electronically different meta and para relationships to the adjacent benzoate units.

MALDI-TOF mass spectrometry measurements demonstrate the incorporation of the desired monomer units into the polymer backbone, as indicated by the matching peak interval (Fig. 4). The observed molecular weight distribution is, however, not representative for polymer **7** because the relative abundance of each molecular ion is dependent on its specific ionization ability, which significantly decreases with increasing molecular weights.



**Figure 3.**  $^{13}\text{C}$  NMR spectrum of polymer **7** (300 MHz, 60,000 scans,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ). The inset shows the region of potential diyne defects.

### Optical Properties

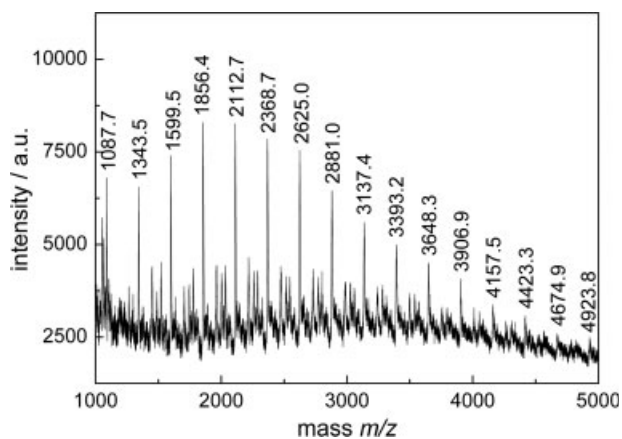
The *ortho*-linked phenylene ethynylene backbone can exist in several different conformations ranging from the extended transoid conformation to the helical cisoid conformation (Fig. 5). An inspection of molecular models suggests a significant difference in the extent of  $\pi$ -conjugation in these two distinct conformations. Although in the planar transoid conformation  $\pi$ -conjugation will reach saturation at an oligomer length of typically several repeat units,<sup>17,29,30</sup> convergence will be reached much more rapidly in the helical cisoid conformation because of significant deviation from planarity limiting the degree of  $\pi$  conjugation.

We anticipated that polymer **7**, appended with the nonpolar side chains, would undergo a solvophobic driven folding reaction in nonpolar solvents. Solvents, such as chloroform, are expected to solvate both the backbone and the side chains, thereby favoring an extended conformation, whereas nonpolar solvents, such as cyclohexane, should preferentially solvate the side chains, causing the conformational transition from an extended structure to a helical structure.

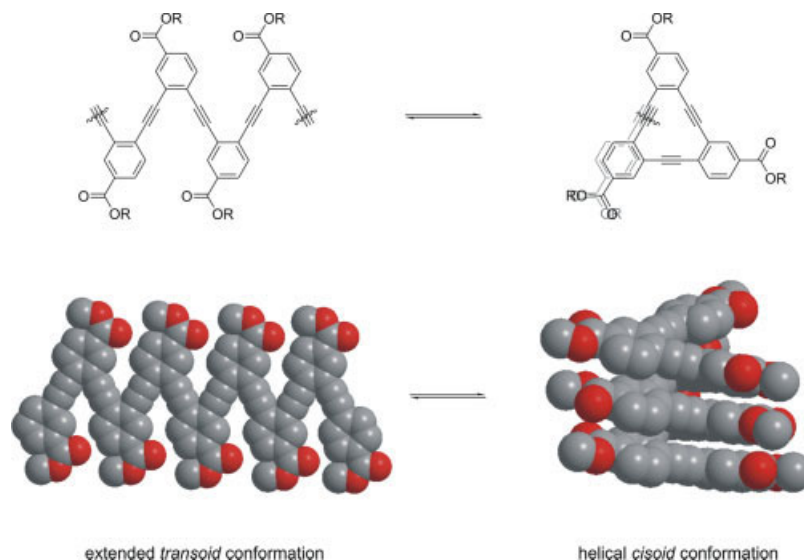
Absorption spectra of polymer **7** in chloroform exhibit a sharp band around 284 nm, which was intuitively assigned to the nonplanar, isolated *ortho*-linked phenylene ethynylene chromophores as the related meta-linked oligomers exhibit a similar optical transition.<sup>4,23</sup> The broad band

extending from 320 to 400 nm is attributed to the planar,  $\pi$ -conjugated, *ortho*-linked phenylene ethynylene repeat units (Fig. 6). However, in the folding-promoting solvent, that is, cyclohexane, the intensity of the broad band, indicative of the extended transoid conformation, diminishes, suggesting an increasing population of the helically folded conformation.

Emission spectroscopy was used to get more insight into the conformational behavior of polymer **7** (Fig. 6). Two emission bands can be observed at 442 and 483 nm in chloroform and at

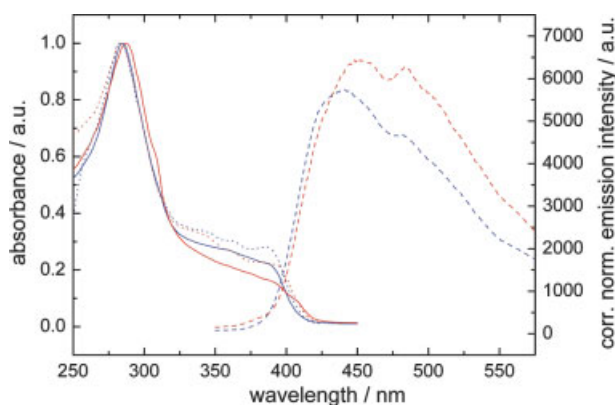


**Figure 4.** MALDI-TOF mass spectrum of polymer **7** (entry 4 in Table 1). The difference between the two adjacent peaks corresponds to the molecular weight of the repeat unit.



**Figure 5.** Comparison of two contrasting backbone conformations: extended transoid conformation leading to efficient  $\pi$  conjugation (left) and helical cisoid conformation leading to inefficient  $\pi$  conjugation (right).

452 and 483 nm in cyclohexane. The position of the emission band is indicative of the extended chromophore.<sup>17,29,30</sup> The redshifted emission at 483 nm presumably arises from the interaction of stacked chromophores leading to a broad excimer-like emission. As expected, this band is more pronounced in the helix-promoting solvent cyclohexane than in chloroform. Solvatochromic effects should not contribute to the hyper/hypochromicity of the relevant absorption and emission bands. Hence, the observed spectral differences in two different solvents independently point to a conformational transition of polymer **7** from an extended structure to a helical structure in



**Figure 6.** (—) UV-vis absorption, (---) emission, and (.....) excitation spectra of polymer **7** in chloroform (blue) and cyclohexane (red) solutions (0.03 mg/mL, 25 °C).

nonpolar solvents. In view of the current data, we are unable to determine the degree of folding.

## CONCLUSIONS

Nonpolar PoPEs have been synthesized via our *in situ* activation/coupling protocol. Microwave irradiation has been found to accelerate the polycondensation reaction, thereby reducing the polycondensation time to 1 h. The resulting polymer has been characterized thoroughly by several analytical methods, including <sup>13</sup>C NMR spectroscopy, which indicates the absence of diyne defects in the polymer structure. The optical spectra, recorded in two different solvents, point to different chain conformations depending on the nature of the solvent. A detailed analysis involving discrete oligomers to elucidate the solution structure of this new foldamer backbone and theoretical work exploring the influence of the conformation on the backbone's electronic properties are currently ongoing.

## REFERENCES AND NOTES

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28. Because of GPC calibration with polystyrene standards, the measured absolute molecular weights are associated with a certain error. Although no experimental proof can be given at this time, we believe that because of their *ortho* connectivity, PoPEs are rather compact, and hence the molecular weights should not substantially be overestimated as in the case of PpPEs [poly(*para*-phenylene ethynylene)s] (see ref. 17).
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