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A Helically folded poly(*m*,*p*-phenylene)

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ABSTRACT

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Keywords: polyphenylenes amphiphilicity helical structures folding Suzuki polycondensation Two amphiphilic poly(*m*,*p*-phenylene)s were synthesized through Suzuki polycondensation from 1,3-phenylene dibromide bearing solubilizing tri- or tetra(ethylene glycol) chains and 1,4phenylene diboronic acid diester. Unlike its tri(ethylene glycol)-functionalized congener the polymer with tetra(ethylene glycol) chains was shown to possess considerably high molecular weight ( $M_w = 15\ 900\ \text{and}\ M_n = 7\ 300$ ) and good solubility in both polar and nonpolar organic solvents. Fluorescence spectra of the polymer recorded in CHCl<sub>3</sub> and aqueous acetonitrile revealed that in the latter solution the fluorescence intensity is considerably lower and the band is redshifted by about 70 nm compared to the former one. This indicates a transition from a random coil conformation to an ordered compact one. A convincing indication of helical folding of the polymer came from an induced circular dichroism spectroscopic study of inclusion complexes of the tubular helical folds with  $\alpha$ -pinene enantiomers influencing the sense of the helix.

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#### 1. Introduction

Helical structures play key roles in a number of biological functions. This fact has inspired chemists to design many helical molecules<sup>1</sup> to investigate their molecular chirality and to use them for practical applications such as chiral materials for asymmetric synthesis,<sup>2</sup> separation of enantiomers,<sup>3</sup> chiral building blocks for self-assembled nanomaterials<sup>4</sup> and devices<sup>5</sup> etc. In this context the design and synthesis of helical polymers and oligomers (foldamers)<sup>6</sup> in which the helix-sense can be controlled is of significant interest. meta-Connected phenylene ethynylene is presently one of the most popular structural type for helical foldamers and polymers. This motif was first developed by Moore and co-workers,<sup>7</sup> who prepared a series of oligo(m-phenylene ethynilene)s and demonstrated their strong tendency to fold into a helical conformation in polar solvents driven by noncovalent solvophobic interactions. This conformation was shown to possess an internal lipophilic cavity capable of guest binding. A helicity of the preferred handedness can be influenced by the formation of inclusion complexes with chiral guests<sup>8</sup> or chiral substituents at the oligomer backbone.<sup>9</sup> The formation of helical structure with a preferred handedness of oligo(m-phenylene ethynylene) foldamers was evidenced by the appearance of pronounced absorption bands in their circular dichroism (CD) spectra. The helix formation along with its absolute of amphiphilic handedness poly(m-phenylene

ethynylene)s equipped with optically active substituents was recently observed directly by means of atomic force microscopy.<sup>10</sup> Although the helical motif on the basis of the *m*phenylene ethynylene structure has proven to be highly valuable in many respects there are a few limitations for practical applicability of oligomers and polymers constructed of these units. Like any other foldamer, oligo(*m*-phenylene ethynylene)s are structurally perfect monodisperse compounds but their multistep synthesis is time-consuming and costly. Additionally, low molecular weight oligomers generally find little use in the production of functional materials. Poly(*m*-phenylene ethynilene)s have the advantages of one-step synthesis and high molecular weights.<sup>11</sup> However, divne defects<sup>12</sup> that are often introduced into the polymer chain during the synthesis would perturb the folding process and disrupt the tubular helical structure. Therefore, it is of importance to develop novel helical polymers with improved structural homogeneity, chemical stability, and functions. Polyarylenes are suitable candidates in this regard since they are chemically and thermally robust. There are a few reports on helical structures formed by oligomeric and polymeric *ortho-* and *meta-*phenylenes.<sup>13,14</sup> These compounds were shown to fold into tight non-tubular helices. However, for applicative purposes, such as catalysis and chiral discrimination, hollow tubular nanostructures are essential. As shown in Figure 1, consideration of molecular models suggests that a polyphenylene comprising alternating meta- and para-phenylene

<sup>†</sup>The article is dedicated to Professor Artem Oganov on the occasion of his 40<sup>th</sup> birthday

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moieties can adopt a tubular helical conformation with an internal diameter of ca. 1 nm. One of us has recently reported the synthesis of high molecular weight poly(m,p-phenylene)s through Suzuki polycondensation.<sup>15</sup> Here we present the synthesis and folding studies of first amphiphilic poly(m,p-phenylene)s.



**Figure 1.**Side (left) and top (right) views of an energy-minimized (MMX force field) helical conformation of an unsubstitutedpoly(*m*,*p*-phenylene) consisting of 96 alternating *m*- and *p*-phenylenes (48 repeat units).

#### 2. Results and Discussion

#### 2.1. Synthesis

A common synthetic route to polyphenylenes consists of Suzuki polycondensation (SPC) of AA and BB types of monomers bearing pairs of aryl halide and arylboronic functionalities, respectively. The synthesis of the AA type monomers **3** is depicted in Scheme 1. The transesterification of commercially available ethyl ester of 3,5-dibromobenzoic acid **1** with monomethyl ethers of oligo(ethylene glycol)s **2** readily gives amphiphilic dibromides **3**. The latter were subjected to SPC with 1,4-phenylene diboronic acid diester **4** (BB-type monomer) under previously reported conditions<sup>15</sup> to yield target poly(*m*,*p*-phenylene)s **5** (Scheme 2).



Scheme 1. Preparation of the AA monomers 3.



Scheme 2. Suzuki polycondensation (SPC) synthesis of amphiphilic polymers 5. Reagents and conditions: Pd[P(*p*-tolyl)<sub>3</sub>]<sub>3</sub>, NaHCO<sub>3</sub>, THF/H<sub>2</sub>O, 80 °C, 96h.

The preparation of polymer 5a turned out to be problematic. The oligomeric product precipitated out from solution during the polymerization. After isolation 5a was found to be largely soluble in chloroform at room temperature. The molecular weight of 5a were determined to be  $M_{\rm w} = 6500 \ (P_{\rm w} = 19)$  and  $M_{\rm n} =$ 2 800 ( $P_n = 8$ ) by GPC analysis relative to retention times of polystyrene standards. The low molecular weight of 5a and its poor solubility in polar solvents preclude the use of the polymer to study helical folding. Unlike the case with 5a, the polycondensation of 3b with 4 proceeded smoothly; no precipitation occurred during the reaction. Polymer 5b was obtained in nearly quantitative yield and subjected to the GPC analysis revealing  $M_w = 15900$  ( $P_w = 41$ ) and  $M_n = 7300$  ( $P_n =$ 19). Notably, according to the molecular model shown in Figure 1, the determined values of molecular weight of **5b** translate to helices with three to seven full turns (one full turn corresponds to six repeat units). Structural integrity of the polymers **5a** and **5b** was confirmed by solution <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (see Figure 2 showing the corresponding spectra of 3b). Elemental analyses of the polymers 5 gave satisfactory convergence with values calculated not including the end groups (see Experimental section).



**Figure 2.** <sup>1</sup>H (a) and <sup>13</sup>C (b) NMR spectra of amphiphilic polyphenylene **5b** recorded in CDCl<sub>3</sub>. The solvent signals are marked (\*).

#### 2.2. Folding studies

The described analyses of the folding of amphiphilic oligo(m-phenylene ethynilene)s revealed that these amphiphilic oligomers exist as random-coiled conformations in chloroform which is a good solvent for both the lipophilic backbone and the oligo(ethylene glycol) chains. The amphiphilic oligomers adopt helical conformations in highly polar solvents that are considered as bad solvents for the nonpolar oligomer backbone. Acetonitrile and its mixtures with water were found to be the best folding-promoting solvents for oligo(m-phenylene ethynylene)s. From a structure standpoint (nonpolar backbone and polar side chains) poly(m,p-phenylene)s **5** are expected to have a similar conformational behavior in the given solvents. Investigation of

solubility of polymers **5** in different solvents showed that polyphenylene **5a** could only be dissolved in chloroform. Its solubility in polar solvents, such as acetonitrile and DMF was found to be very poor. On the contrary, polyphenylene **5b** exhibited good solubility in both chloroform and the polar solvents. At concentrations of up to 100 mg·L<sup>-1</sup> the polymer was also soluble in an acetonitrile-water (80:20) solution. However, an attempt at increasing the water content in the acetonitrile solution caused precipitation of the polymer. The decreased solubility of **5b** in aqueous acetonitrile compared to that of *m*phenylene ethynylene oligomers is understood taking into account a larger liphophilic load in the backbone of the former (six carbons in *p*-phenylene vs. two carbons in acetylene linkage). On the basis of the solubility analysis, all further studies were performed with polyphenylene **5b**.

UV-spectroscopic measurements of polyphenylene **5b** carried out in different solvents (CHCl<sub>3</sub>, THF, DMF, CH<sub>3</sub>CN, aqueous CH<sub>3</sub>CN) reveal that the absorption maximum of the polymer does not depend much on the solvent nature; all observed absorption maxima lie in the range from 286 to 292 nm. Figure 3 depicts UV spectra of **5b** recorded in pure acetonitrile and in an acetonitrilewater (80:20) solution. These absorption maxima differing by only 6 nm are the two "extreme" cases.

 $\begin{array}{c} 0.5 \\ \uparrow 0.4 \\ A/a.u. \\ 0.3 \\ 0.2 \\ 0.1 \\ \hline \\ 240 \\ 260 \\ 280 \\ 300 \\ 320 \\ 340 \\ 360 \\ 380 \\ \lambda/ \text{ nm} \end{array}$ 

**Figure 3.** UV spectra of polyphenylene **5b** (10 mg·L<sup>-1</sup>) in acetonitrile (solid line,  $\lambda$ max = 286 nm) and in an acetonitrile-water 80:20 solution (dashed line,  $\lambda$ max = 292 nm).



**Figure 4.** Fluorescence spectra of polyphenylene **5b** ( $10 \text{ mg} \cdot \text{L}^{-1}$ ) in chloroform (solid line) and in an acetonitrile-water (80:20) solution (dashed line). Excitation at 290 nm.

Notably, conformational transitions, such as coil-to-helix, are rarely evident from the UV spectra of amphiphilic foldamers.

Fluorescence spectroscopy was shown to be a valuable tool for study of conformational changes of *m*-phenylene ethynylenes.<sup>16</sup> Therefore, for further conclusions on the conformation of **5b** its fluorescence spectra were recorded.

As shown in Figure 4, the fluorescence intensity of 5b in aqueous acetonitrile is considerably smaller than that in chloroform. In addition the fluorescence emission band of the aqueous acetonitrile sample is redshifted by about 70 nm. Both the decreased fluorescence intensity and the redshift are indicative of the compact folded conformation of 5b in aqueous acetonitrile. After the excitation, the photons emitted by the phenylene chromophores of 5b in its folded state could get efficiently absorbed by the phenylene units of spatially adjacent helical turns leading to the emission decrease. The maximum at 425 nm (the redshift compared with the chloroform sample) can be attributed to  $\pi$ -stacked aromatic chromophores,<sup>17</sup> which is also in line with the assumption of the helically folded conformation of 5b. The fluorescence spectrum of 5b in chloroform indicates an unfolded random coiled structure in which chromophore units interact more with the solvent rather than with each other resulting in efficient emission at a shorter wavelength.



**Figure 5.** CD spectra of the polyphenylene **5b** (10 mg·L<sup>-1</sup>) in an acetonitrilewater solution (80:20). Dashed line corresponds to the solution of the pure polymer. Solid line is the spectrum of the polymer in the presence of (1*S*)-(–)- $\alpha$ -pinene; dotted line is the spectrum of the polymer in the presence of (1*R*)-(+)- $\alpha$ -pinene. The concentration of  $\alpha$ -pinene in the solutions was 5 µmol·L<sup>-1</sup> that corresponded to a ratio of one  $\alpha$ -pinene per one full helical turn (6 repeat units).

As follows from the molecular modeling (Figure 1) the helically folded poly(m,p-phenylene) should possess an internal cavity with a diameter ca. 1 nm. The cavity is hydrophobic and, therefore, suitable for nonpolar guests of matching size. An inclusion of a chiral guest should lead to a formation of two diastereoisomeric complexes with R and S helices. Assuming that in the solution there is a thermodynamic equilibrium between the R and S helices, the binding of the chiral guest would shift the equilibrium to an energetically more favored diastereoisomeric complex. The prevailing handedness of the helix should manifest itself in CD spectra. Indeed, the addition of optically pure  $\alpha$ -pinene enantiomers to dilute solutions of polyphenylene **5b** in aqueous acetonitrile results in induced circular dichroism. Figure 5 shows the CD spectra of **5b** in presence of both  $\alpha$ -pinene enantiomers. The control CD measurements of the pure **5b** did

not reveal any absorbance (the dashed line in Figure 5). Noteworthy,  $\alpha$ -pinene does not absorb in this wavelength region.<sup>8a</sup> Therefore, the observed bands in the CD spectra originate from the helical conformation of the polyphenylene chain.

#### 3. Conclusions and outlook

Amphiphilic poly(*m*,*p*-phenylene) **5b** presented here is a novel structural motif capable of helical folding through solvophobic interactions. Molecular modeling reveals that the helices made up of the poly(*m*,*p*-phenylene) are tubular structures with lipophilic internal cavity. According to the molecular weight distribution measured by GPC the polymer can form helices with three to seven full turns (assuming one turn consists of six repeat units). The folding into helical conformation occurs in dilute solutions of the polymer in aqueous acetonitrile and manifests itself best through induced circular dichroism spectroscopy of the inclusion complexes of tubular helical folds with enantiomers of a-pinene. The addition of an optically pure  $\alpha$ -pinene shifts the equilibrium between R and S helices toward the one that forms a more stable diastereoisometric inclusion complex with the given  $\alpha$ -pinene enantiomer. The increased population of helices of one handedness is reflected by a pronounced CD activity. Fluorescence spectroscopy is also indicative of the coil-to-helix conformational transition of the polymer in aqueous acetonitrile.

Ongoing work in our laboratory is concerned with the design of monomers for the synthesis of poly(m,p-phenylene)s with higher molecular weights and an improved hydrophilic-lipophilic balance. The ability to control the helix sense of high molecular weight tubular structures might be of importance not only on account of their chirality-oriented applications but also to keep the uniform shape of the cylindrical nanoobjects, as schematically shown in Figure 7.



**Figure 6.** Possible mechanisms of helical folding of amphiphilic polyphenylenes in chiral (A) and achiral (B) environments. The cartoon representation of the polymer is based on a molecular model of poly(*m*,*p*-phenylene) consisting of 60 repeat units. In a long polymer chain the folding can occur independently at several places of the chain. Furthermore, in case of folding in an achiral environment the local helical folds of one polymer chain may have different handedness.

One can easily imagine the transition of a random coil conformation of a high molecular weight helically foldable polymer into a helical conformation that starts independently at different sites of the macromolecule. In this case an uncontrolled (with no chiral auxiliary present) folding may lead to the formation of multiple local helical folds of arbitrary handedness resulting in a distorted secondary structure, as illustrated in Figure 7, path B. In an alternative situation in which the folding is guided by an asymmetric support, *e.g.*, chiral guest, solvent, or a substituent, the formation of a uniform secondary structure is more feasible (Figure 7, path A).

#### 4.1. General

4. Experimental section

NMR spectra were recorded on Bruker Avance 300 and Bruker Avance 500 spectrometers. TMS was used as an internal standard. MALDI-TOF measurements were carried out using a Bruker Ultraflex II mass spectrometer. UV/VIS measurements were performed on a Perkin Elmer Lambda 20 UV/VIS spectrometer at 20 °C in 1cm thick quartz cuvettes. Fluorescence spectra were recorded on a Spex 1681 spectrometer at room temperature in 1 cm thick quartz cuvettes.Circular dichroism (CD) spectra were recorded on a Jasco, J-715 spectropolarimeter at 25 °C.

Analytical GPC measurements in chloroform as eluent were performed at room temperature at a flow rate of 1.0 mL/min. The column set consisted of SDV columns, and the detectors used were UV and RI. Polystyrene standards were used for the calibration. A Viscotek GPC-System equipped with a pump, a degasser (GPCmax VE2001), RI detector (302 TDA), and three columns (2×PLGel Mix-C and ViscoGEL GMHHRN 18055, 7.5×300 mm each) was used. Given GPC data refere to low angle light scattering measurement. Elemental analysis was performed on a Leco 900 instrument.

Note, the slightly excessive deviations between the calculated and measured values in elemental analyses of carbon in polymers **5a** and **5b** are associated with the polymers' end groups. Given the not fully clarified nature and the amount of the latter, we neglected them in the calculated values of elemental analyses.

# 4.2. 2-(2-(2-Methoxyethoxy)ethoxy)ethyl 3,5-dibromobenzoate (3a)

A suspension of ethyl 3,5-dibromobenzoate 1 (6.8 g, 21.17 mmol), 2-(2- (2-methoxyethoxy)ethoxy)ethanol 2a (18.3 g, 111.0 mmol) and potassium carbonate (1.0 g, 7.24 mmol) was heated at 85 °C in a distillation system as long as the condensation of ethanol was complete. The excess of ether 2a was removed by distillation under reduced pressure. The residue was subjected to flash chromatography with ethyl acetate/hexane (1:1) as eluent to give upon evaporation 6.27 g (65%) of colorless oil. [Found: C, 39.39; H, 4.42; C<sub>14</sub>H<sub>18</sub>Br<sub>2</sub>O<sub>5</sub> requires C 39.66, H 4.28%]; R<sub>f</sub> (ethyl acetate/hexane 1:1) = 0.2;  $v_{max}$  (liquid film) 3130-3055 (ArH), 2820 (CH), 1729 (C=O), 1120, 1127 (C-O), 1075 (ArBr)  $cm^{-1}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 3.29 (s, 3H, OCH<sub>3</sub>), 3.46 (t, 2H, J 3.66 Hz, OCH<sub>2</sub>), 3.58. -3.63 (m, 6H, OCH<sub>2</sub>), 3.76 (t, 2H, J 4.17 Hz, OCH<sub>2</sub>), 4.41 (t, 2H, J 4.28 Hz, OCH<sub>2</sub>), 7.75 (t, J 1.8 Hz, 1H, ArH), 8.01 (s, 2H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 200 MHz); δ (ppm): 59.00, 64.81, 68.96, 70.59, 70.61, 70.66, 71.92, 122.94, 131.38, 133.31, 138.21, 163.89; *m/z* (LC-MS, APCI): M+, found 424. C<sub>14</sub>H<sub>18</sub>Br<sub>2</sub>O<sub>5</sub> requires 423.93.

#### 4.3. 2,5,8,11-Tetraoxatridecan-13-yl 3,5-dibromobenzoate (3b)

A suspension of ethyl 3,5-dibromobenzoate 1 (24.62 g, 15.0 mmol), 2,5,8,11-tetraoxatridecan-13-ol 2b (15.62 g, 75.0 mmol), and potassium carbonate (0.52 g, 37.5 mmol) was heated at 85 °C in a distillation system as long as the condensation of ethanol was complete. The excess of ether **2b** was removed by distillation under reduced pressure. The residue was subjected to flash chromatography with ethyl acetate/hexane (1:1) as eluent to give upon evaporation 3.1 g (44%) of colorless oil. [Found: C, 40.75; H, 4.70; C<sub>16</sub>H<sub>22</sub>Br<sub>2</sub>O<sub>6</sub> requires C 40.88, H 4.72%]; R<sub>f</sub> (ethyl acetate/hexane 1:1) = 0.15; v<sub>max</sub> (liquid film) 3133–3057 (ArH), 2822 (CH), 1721 (C=O), 1115, 1126 (C-O), 1069 (ArBr) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 3.41 (s, 3H, OC<u>H<sub>3</sub></u>), 3.53–3.58 (m, 2 H, OC<u>H<sub>2</sub></u>), 3.60–3.73 (m, 10 H, OC<u>H<sub>2</sub></u>), 3.87 (t, 2H, J 4.8

Hz, OC<u>H<sub>2</sub></u>), 4.51 (t, 2H, *J* 3.8 Hz, OC<u>H<sub>2</sub></u>), 7.88 (t, 1H, *J* 1.8Hz, Ar<u>H</u>), 8.15 (d, 2H, *J* 1.8 Hz, Ar<u>H</u>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  (ppm): 59.00, 64.84, 68.96, 70.51, 70.62, 70.64, 71.92, 122.96, 131.39, 133.32, 138.23, 163.92; *m/z* (LC-MS, APCI): M+, found 468. C<sub>16</sub>H<sub>22</sub>Br<sub>2</sub>O<sub>6</sub> requires 467.98.

#### 4.4. *Poly*[2-(2-(2-*methoxyethoxy*)*ethoxy*)*ethyl* 4',5-*biphenyl*-3*carboxylate*] (**5a**)

Dibromide 3a (2 g, 4.5 mmol) and benzene-1,4-bis(boronic acid)propane-1,3-diol diester 4 (4.5 mmol) were dissolved in dry THF (100 mL). A concentrated solution of NaHCO<sub>3</sub> in water (30 mL) was added to the reaction mixture and the system was degassed. Freshly prepared  $Pd[P(p-tolyl)_3]_3^{15}$  (3 mg, 0.6 mol%) was added and the reaction mixture was allowed to stir at 80 °C for 96 h under nitrogen atmosphere. Then deionized water (200 mL) was added and the emulsion was taken up with dichloromethane (2×150 mL). The organic layer was separated, washed with water, brine, dried over Mg<sub>2</sub>SO<sub>4</sub>, and evaporated to give 0.97 g (60%) of polyphenylene 5a as colorless solid. [Found: C, 69.44; H, 6.60; C<sub>20</sub>H<sub>22</sub>O<sub>5</sub> requires C 70.15, H 6.48%]; v<sub>max</sub> (KBr) 3154–3072 (br, ArH), 2800 (CH), 1690 (C=O), 1111, (C-O); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  (ppm): 3.37 (br. s, 3H, OCH<sub>3</sub>), 3.52 (br. s, 2H, OCH<sub>2</sub>), 3.72 (br. s, 6H, OCH<sub>2</sub>), 3.94 (br. s, 2H, OCH<sub>2</sub>), 4.62 (br. s, 2H, C(O)OCH<sub>2</sub>), 7.89 (br. s, 4H, ArH), 8.17 (br. s, 1H, ArH), 8.40 (br. s, 2H, ArH);<sup>13</sup>C NMR (CDCl<sub>3</sub>, 175 MHz) δ(ppm): 59.00, 64.81, 68.96, 70.59, 70.61, 70.66, 71.92,128.00, 128.29, 130.87, 131.90, 140.22, 141.94, 167.03.

# 4.5. *Poly*[2,5,8,11-*tetraoxatridecan-13-yl* 4',5- *biphenyl-3* - *carboxylate*] (**5b**)

Dibromide 3b (1.01 g, 2.14 mmol) and benzene-1,4bis(boronic acid)propane-1,3-diol diester 4 (0.526 g, 2.14 mmol) were dissolved in dry THF (50 mL). A concentrated solution of NaHCO<sub>3</sub> in water (10 mL) was added to the reaction mixture and the system was degassed. Freshly prepared  $Pd[P(p-tolyl)_3]_3$  (1.5) mg, 0.6 mol%) was added and the reaction mixture was allowed to stir at 80 °C for 96 h under nitrogen atmosphere. Then deionized water (100 mL) was added and the emulsion was taken up with dichloromethane (2×70 mL). The organic layer was separated, washed with water, brine, dried over Mg<sub>2</sub>SO<sub>4</sub>, and evaporated to give a highly viscous residue. The latter was dissolved in chloroform (10 mL) and the solution was poured into stirred hexane (100 mL). The suspended polymer was separated by centrifugation as colorless solid. [Found: C, 67.86; H, 6.93; C<sub>22</sub>H<sub>26</sub>O<sub>6</sub> requires C 68.37, H 6.78%]; v<sub>max</sub> (KBr) 3160-3066 (br, ArH), 2807 (CH), 1695 (C=O), 1110 (C-O); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ (ppm): 3.43 (br. s, 3H, OCH<sub>3</sub>), 3.52 (br. s, 2H, OCH<sub>2</sub>), 3.61 (br. s, 2H, OCH<sub>2</sub>), 3.64 (br. s, 2H, OCH<sub>2</sub>), 3.69 (br. 2H, OCH<sub>2</sub>), 3.72 (br. s, 2H, OCH<sub>2</sub>), 3.76 (br. s 2H, OCH<sub>2</sub>), 3.93 (br. 2H, OCH<sub>2</sub>), 4.60 (br. s, 2H, C(O)OCH<sub>2</sub>), 7.87 (br. 4H, Ar $\underline{H}$ ), 8.15 (br. s, 1H, Ar $\underline{H}$ ), 8.38 (br. s, 2H, Ar $\underline{H}$ ); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz) δ (ppm): 58.96, 64.43, 69.26, 70.49, 70.65, 71. 89, 127.35, 127.88, 130.14, 131.51, 139.67, 141.54, 166.39.

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#### Supplementary data

Supplementary data (GPC elution curves for compounds **5a** and **5b**) associated with this article can be found, in the online version, at:

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## SUPPLEMENTARY DATA

## A Helically folded poly(*m*,*p*-phenylene)

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### GPC of polyphenylene 5a



### GPC of polyphenylene 5b



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