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Conformational Changes of Facially Amphiphilic *meta*-Poly(phenylene ethynylene)s in Aqueous Solution

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ABSTRACT: Design and control of polymer secondary conformation is a challenging problem. Facially amphiphilic polymers based on rigid but conformationally flexible *meta*-phenylene ethynylene backbones were prepared and characterized in solution. It was found that these polymers undergo different conformational changes based on the presence or absence of an alkyl side chain when the solvent was changed from DMSO to 90% H_2O/DMSO. This report focuses on the architecture without an alkyl substituent, which appears to adopt a helical conformation.

Introduction

Many natural molecules take on different conformations depending on their environment and sequence. These conformations can be stabilized by noncovalent interactions such as hydrogen bonding, the hydrophobic effect, or van der Waals forces.[1] A challenging but interesting problem is faced when trying to prepare synthetic, nonbiological molecules that will react similarly to changes in their environment. Success in this area may provide a simpler model for complex macromolecules and lead to insight regarding the formation of secondary, tertiary, and quaternary structures of natural molecules. Although folded structures induced by specific metal−ligand and hydrogen bonding have been widely studied,[2−6] there are only a few reports on the use of solvophobic[7−9] or $\pi-\pi$ stacking interactions[10,11] to control conformation. Alternately, it is known that when traditional synthetic macromolecules, such as polymers, are placed in poor solvents, they form collapsed, dense globular structures lacking well-defined order, and when placed in a good solvent the molecules assume an expanded, random coil structure but still lack internal order.[12,13]

There has been recent interest in molecules that form well-defined, ordered structures in solution.[14−16] Fleet and co-workers synthesized oligomers of furanose with only four repeat units that adopt secondary structures held together by hydrogen bonding.[17] β-Amino acid oligomers as short as six residues have been reported to form stable helices.[18,19] Zuckermann and co-workers synthesized oligo-N-substituted glycines of various lengths, and despite the achirality of the backbone and the lack of internal hydrogen bonds, these molecules form helical structures.[20] In addition, aromatic amides adopt well-defined crescent and helical structures.[21−25] A common theme of this research is that the molecules studied are discrete oligomers where the structure can be controlled by changes in temperature or pH.

Moore and co-workers reported aromatic hydrocarbon backbones based on *meta*-phenylene ethynylene (*m*-PE) in which solvent was used to influence an extended random coil or helical structure.[8,9,26] By attaching polar triethylene glycol side chains to the nonpolar *m*-PE backbone, high dielectric constant solvents induce collapsed (helical) structures which minimize solvent−backbone interactions while maximizing solvent−side chain contacts. Structural investigations into helix stability have included the addition of methyl groups[27] and metal−ligands[6] to the helix interior, aromatic ring electronics,[8] and hydrogen bonding.[28] By manipulating the linker functionality between the ethylene glycol chain and the PE backbone, it is possible to influence the stability of the collapsed, helical structure in solution.[8,29] The coil−helix folding transition of these oligomers has been conveniently monitored by UV−vis and fluorescence spectroscopy[8,29] and confirmed by chiral guest-induced circular dichroism.[27] Like other studies on folding oligomers, only discrete chain length *m*-PEs have been studied so that the influence of molecular weight polydispersity is not known.

We have been interested in the study of facially amphiphilic polymers based on *meta*-poly(phenylene ethynylene)s[30] (*m*-PPE), and Langmuir experiments performed on these molecules confirmed their amphiphilicity at the air−water interface by adopting an extended structure.[31] During this research, we observed a clear difference in properties between facially amphiphilic *m*-PPEs with and without alkyl side chains. The fact that molecules of *m*-PPE lacking an alkyl side chain consistently provided different results from those with an alkyl substituent prompted us to investigate the possibility of helix formation in polymeric *m*-PPEs with cationic, polar side chains. The alkyl side chain would be located in the helix interior upon folding, and the absence of this group would allow helix formation.

Experimental Section

The synthesis of polymers **1** and **2** followed previously reported procedures, and polymers **3** and **4** were synthesized using similar procedures.[30] ^{1}H and ^{13}C NMR spectra were obtained at 300 MHz with a Bruker DPX-300 NMR spectrometer. The gel permeation chromatography (GPC) experiment was performed in THF at room temperature using a PL LC 1120 pump, a Waters R403 differential refractometer, and three PLgel columns (10^5, 10^4, and 10^3 Å). The system was calibrated with polystyrene standards. Absorption spectra were measured on a Hewlett-Packard 8453 spectrophotometer. Emission and excitation spectra were taken on a Perkin-Elmer LS 50B spectrometer with a xenon lamp light source.

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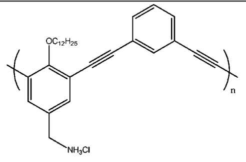
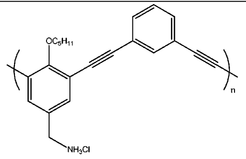
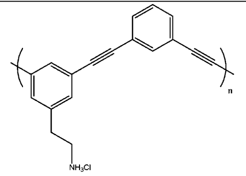
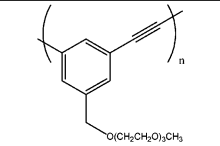
Table 1. *m*-PPE Polymers Used in This Study and Their Molecular Weight Analysis

Polymer	Structure	Mn	PDI	n*	corrected n†
1		8,420	1.40	16	8
2		8,450	1.31	20	10
3		6,760	1.48	20	10
4		10,900	1.53	31	16

* These values are based on GPC data calibrated to polystyrene standards.

† The corrected n values are based on MALDI-ToF data for polymer **2**.

To determine the corrected $n^{\dagger}$ values listed in Table 1, **2** was fractionated by the GPC. Refractive index detector was used to monitor peak elution, and 0.3 mL fractions were collected during the elution, totaling 20 samples. These fractions were then analyzed by MALDI-ToF. The fraction that included the top of the peak, as determined by GPC, was used to calculate $n^{\dagger}$. These data were obtained at the University of Massachusetts Amherst mass spec facility, which is supported in part by the National Science Foundation.

The fluorescence and UV−vis were monitored with increasing percentage of water. A stock solution of polymer was made in DMSO as to keep the polymer concentration constant throughout the experiment. The concentrations explored ranged from 50 to 5000 μg/mL to test for concentration independence. For fluorescence, the samples were prepared at a concentration where the UV absorbance was less that 0.1 so that inner filter effects were minimal. For UV spectra, the OD values were around 0.75.

Circular dichroism (CD) was monitored on a JASCO J720 spectrometer at ambient temperature in 0.1 cm rectangular quartz cuvettes using concentrations of 0.100 mg/mL. The concentration of polymer and the number of equivalents (100) of the chiral acid were calculated on the basis of molecular weight of the monomer unit.

Results and Discussion

Both helical and extended structures of *meta*-phenylene ethynylenes have been observed, confirming the rich conformational flexibility available from this molecular backbone. Helical structures were driven by solvophobic collapse[8,9] while extended conformations are governed by patterning of polar and nonpolar side chains[31,32] or the reduction of free volume in the solid state.[33,34] The four polymers discussed in this paper are shown in Table 1 along with molecular weight information based on GPC standards and MALDI-ToF experiments. Polymers **1**, **2**, and **3** contain polar groups with cationic amines while **4** has triethylene glycol side chains. In addition, **1** and **2** have nonpolar alkyl side chains in contrast to **3** and **4**. Polymer **4** was prepared in order to make direct comparisons to Moore's structure, although **4** is a polydisperse sample while Moore studied discrete oligomers.[8]

When studying the aggregation behavior of facially amphiphilic *m*-PPEs **1** and **2**, fluorescence spectroscopy showed small wavelength shifts (~10 nm) upon the addition of water which is consistent with intermolecular distances of ~4.9 Å.[35] Much larger red shifts would be expected for a highly collapsed structure with aromatic distances less than 4.5 Å.[29,35−38] For polymers **1** and **2**, DMSO appears to be a good solvent in which the polymer adopts a random coil conformation based on NMR, absorption, and emission spectroscopy, while water is a poor solvent resulting in precipitation of polymers **1** and **2** at high water content.

Figure 1 shows the fluorescence spectra of polymers **1** and **3** in two different solvents, DMSO and 90% H_2O/DMSO, while keeping the polymer concentration constant. The spectra for **1** (Figure 1a) have an intense peak in DMSO; however, as water is added up to 90% H_2O/DMSO, the emission spectra decreases in intensity, broadens, and red shifts slightly by 10 nm. In contrast, when similar experiments were performed with **3**, very different spectra were obtained in 90% H_2O/DMSO compared to those of polymers **1** and **2**.[30] The fluorescence spectrum of polymer **3** has an intense peak in DMSO with $\lambda_{\max}$ of 383 nm compared to **1** at 377 nm but broader than that observed for **1** by 40 nm at full width half-height (fwhh). The small differences in $\lambda_{\max}$ can be explained by electron density of the two polymers since **3** does not have the ether substituent of **1**. The increase in width at fwhh observed for **3** may indicate that DMSO is a better solvent for **1**, which might not be surprising given the absence of the alkyl side chain in **3**.[39] This is further supported by the spectrum obtained in 95% chloroform/DMSO in which $\lambda_{\max}$ is 381 nm; however, the peak is substantially narrower than those obtained in DMSO.[39] This suggests the DMSO spectrum may be a combination of those observed in 95% $CHCl_3$/DMSO and 90% H_2O/DMSO. Upon changing to 90% H_2O/DMSO, the signal for **3** decreases intensity and red shifts approximately 50 nm. This broad, featureless red-shifted band can be explained by close $\pi-\pi$ stacking of the aromatic rings.[29] Regardless, the changes are consistent with spectra obtained by Moore and coworkers for helical conformations;[29] however, random collapse, to provide close aromatic contacts without helix formation, could also give rise to these observations.[40] The differences observed in the emission spectra between **1** and **3** in 90% H_2O/DMSO strongly suggest different conformational or aggregational modes are present.

In fact, conformational changes are more likely than aggregation on the basis of the observation that **1** precipitated from 90% H_2O/DMSO solutions at 50 μg/mL after 2 days while **3** remains soluble in this solvent at 100 times the concentration (5000 μg/mL) over months. Polymer **2** is also observed to precipitate from 90% H_2O/DMSO solutions after 2 days at concentrations of 50 μg/mL. Polymer **1** is believed to aggregate through an extended amphiphilic structure[31] organized into layers,[32] which is likely to give macroscopic precipitation as more molecules are added to the aggregate. Interestingly, the lack of precipitation from **3** in 90% H_2O/DMSO would indicate random collapse of the polymer chains

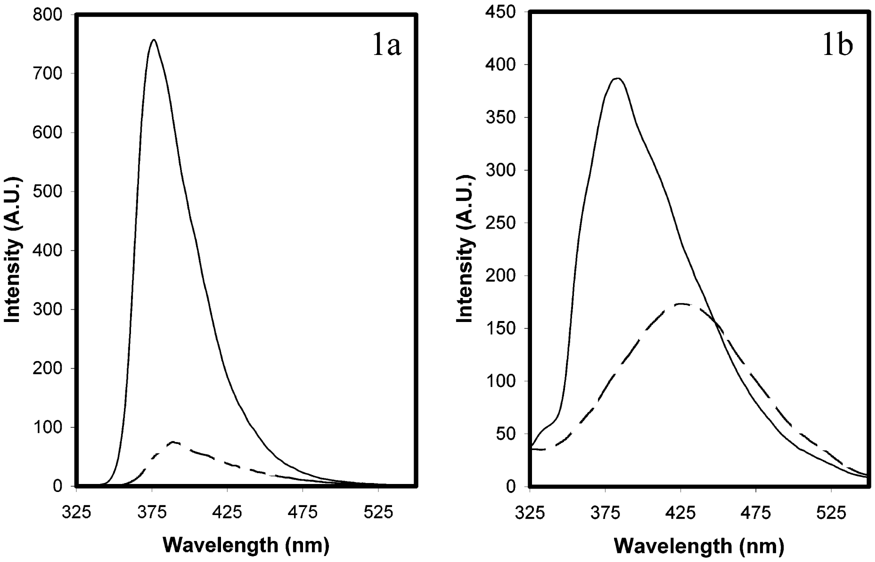


Figure 1. Fluorescence spectra of polymer **1** (a) and polymer **3** (b) in DMSO (solid) and 90% H_2O/DMSO (dashed). The concentrations of **1** and **3** were held constant within each experiment so direct comparison of intensity can be made.

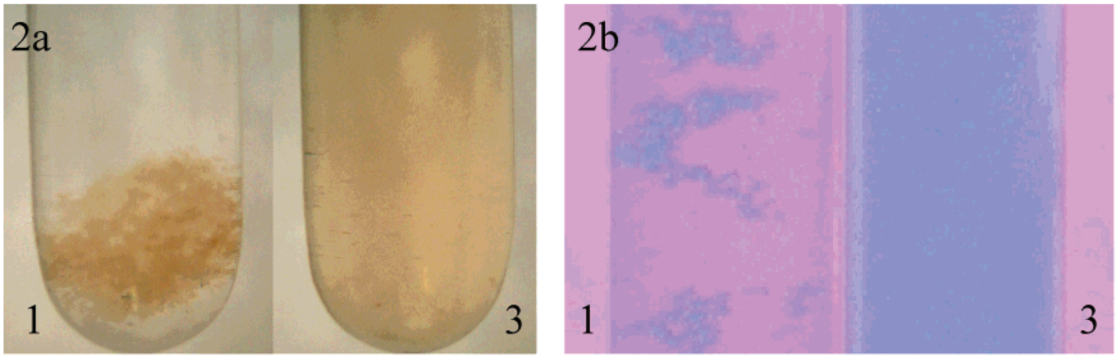


Figure 2. Pictures of polymer **1** (left) and **3** (right) in (a) natural light and (b) long wave UV light. Notice the differences in the solution. Polymer **1** has a turbid nature with visible aggregates while **3** remains optically clear.

is not responsible for the changes observed by fluorescence spectroscopy since this is expected to result in precipitation over time.[41]

Shown in Figure 2a are photographs of polymers **1** and **3** in 90% H_2O/DMSO solution taken under natural light in which **1** has precipitated out of solution while polymer **3** is still optically clear and in solution as observed by the slight yellow color due to the higher concentration of polymer. Figure 2b was taken under long wavelength UV illumination and shows that only the particles formed by precipitation of **1** fluoresce while **3** shows homogeneous emission from the solution. The lack of precipitate from **3** but dramatic change observed in the emission spectra suggests this polymer adopts a new conformation in 90% H_2O/DMSO which is quite different from **1** and would be consistent with intramolecular helix formation. It is clear that **1** cannot adopt helical conformations because three dodecyloxy side chains are much too large for the interior cavity formed by the helix while **3** does not have this steric problem due to the lack of alkyl side chains. It is also possible that **3** adopts some other structure by intermolecular self-assembly which does not lead to macroscopic precipitation. For example, the formation of cylindrical micelle-like structures[42,43] in which the polymer backbone extends along the cylinder length cannot be ruled out. However, this is not consistent with close $\pi-\pi$ stacking suggested by the emission spectrum. Initial ^1H NMR investigations have not provided insight into these changes, and vapor pressure osmometry cannot be performed in DMSO[44] to measure an increase in molecular weight due to intermolecular aggregation.

UV–vis spectroscopy has proven extremely beneficial for characterizing the random coil to helix folding reaction in *m*-PEs by monitoring the relative populations of transoid and cisoid confirmations, respectively.[29] Moore and co-workers were able to produce sigmoidal titration curves from discrete *m*-PE oligomers with triethylene glycol ester side chains by monitoring the ratio of peaks at 289 and 305 nm as the solvent was changed from acetonitrile to chloroform. In their system, strongly cooperative unfolding is seen for oligomers longer than 12 units, while broad noncooperative transitions are seen for shorter chain lengths. Most of their work has focused on ester *m*-PE derivatives, although the influence of aromatic ring electron density was investigated.[29] For benzyl ethers, similar to **4**, UV–vis and emission spectra were consistent with helix formation, but no titration curves were provided. In this regard, we examined UV–vis titration curves of **3** in DMSO and water as well as the polymeric analogue of Moore's triethylene glycol benzyl ether, **4**, in chloroform and acetonitrile. The insets of parts a and b of Figure 3 show UV–vis curves for **3** in DMSO and 90% H_2O/DMSO and **4** in chloroform and 90% acetonitrile/

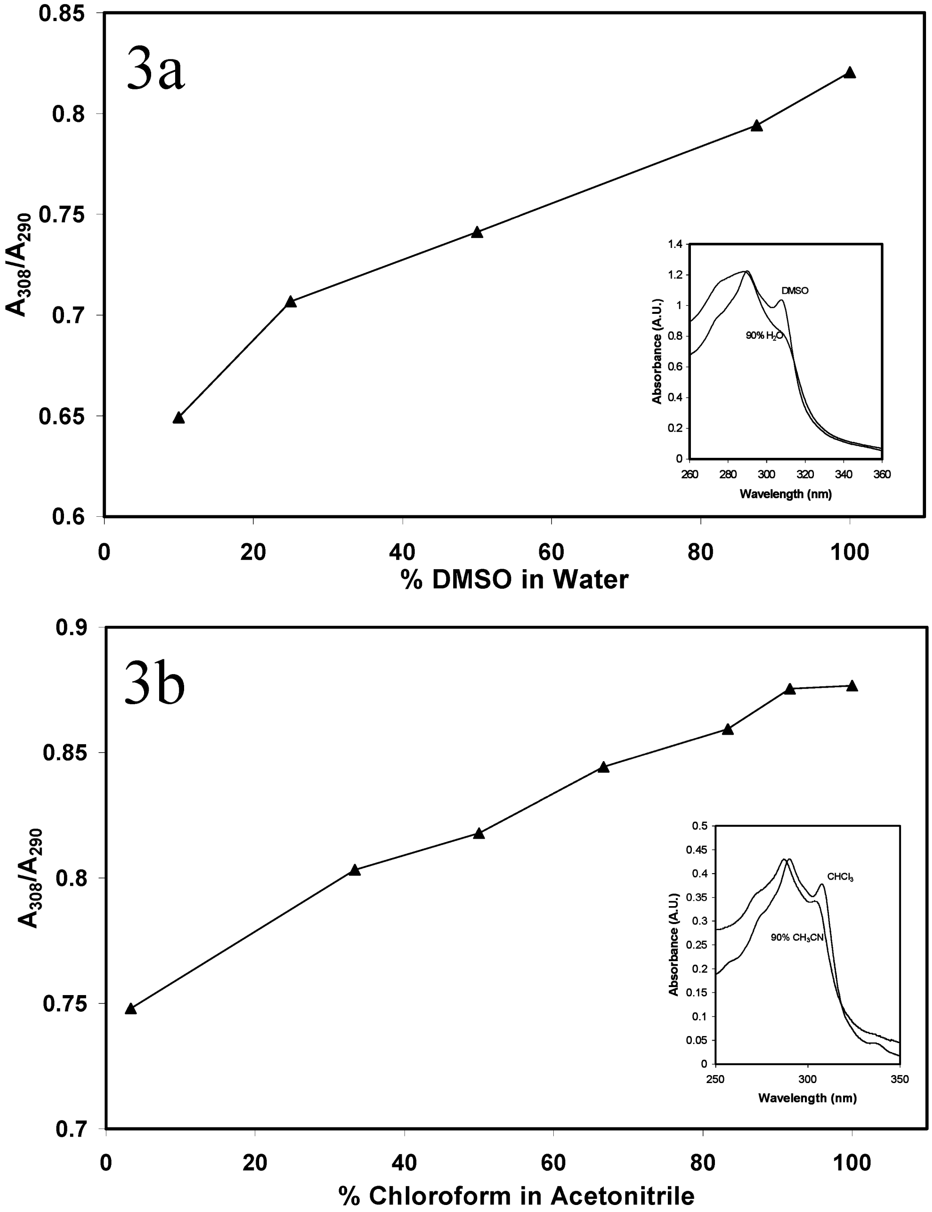


Figure 3. (a) Titration curve for polymer **3** when changing solvents from DMSO to 90% H_2O/DMSO. The inset shows the absorbance spectra for polymer **3** at the beginning and end points of the curve. (b) Titration curve for polymer **4** when changing solvents from $CHCl_3$ to 90% $CH_3CN/CHCl_3$. The inset shows the absorbance spectra for polymer **4** at the beginning and end points of the curve.

chloroform, respectively. These end points show the characteristic changes observed for the coil-to-helix transitions of *m*-PE, which in Moore's work have been confirmed by circular dichroism spectroscopy (CD).[27] However, titration curves shown in parts a and b of Figure 3 for **2** and **4**, respectively, do not show cooperative unfolding reactions. The lack of a distinct transition may be due to the relatively low molecular weight of these polymers so that large populations of short chains are present. These short chains would contribute significantly to a noncooperative transition as observed by Moore for discrete oligomers of 8 and 10 repeats. The reported molecular weights are referenced to polystyrene standards, which are known to overestimate the molecular weight of rigid polymers by 1.5−2.0.[45−48] In addition, MALDI-ToF spectra were obtained by fractionation of the GPC peak and suggest the molecular weights are between 0.5 and 0.6, the value obtained from GPC. The kind of transitions observed in Figure 3 have also been attributed to multichain interactions;[49] however, it is believed that, in this case, it is intramolecular folding since the results are independent of time and concentration (50−5000 μg/mL). In addition, intermolecular associations, like those to form cylindrical micelles, would not be expected to increase the population of cisoid conformations as observed by the UV−vis experiments. Also, Moore and co-workers report that the oligomer of polymer **4** needs a more polar solvent (i.e., water) in order to undergo a strong transition in UV and fluorescence spectroscopy;[8] however, **4** is not soluble in neat acetonitrile so that addition of water cannot be performed due to the presence of chloroform.

From UV−vis titration curves, changes in 308/290 ratio, and emission in polar solvents, a helical conformation of **3** cannot be firmly concluded. As a result, CD experiments were performed; however, **3** does not contain any chiral centers, and so an equal population of right- and left-handed helical conformations would

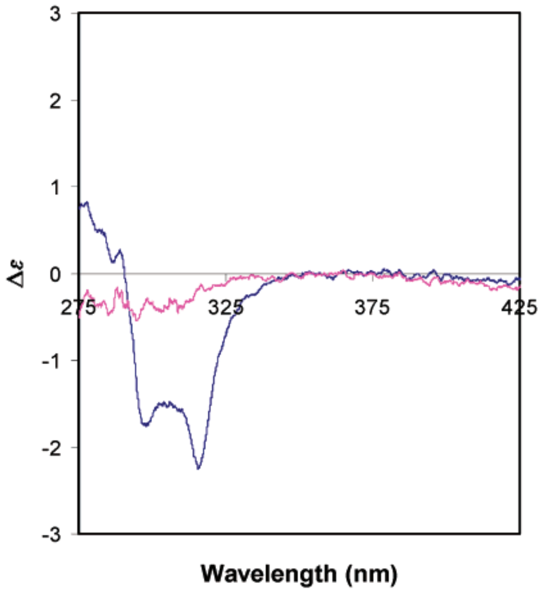


Figure 4. Circular dichroism spectra of **3** in DMSO (red line) and 90% H_2O/DMSO (blue line) with D-mandelic acid (100 equiv). The appearance of a signal only in 90% H_2O/DMSO suggests a helical conformation is likely.

be expected. Chiral additives have been used previously to induce a preference of one-handedness in helical structures.[50] Therefore, we speculated that the addition of chiral carboxylic acids could result in associations with the primary amines of **3** and influence helical handedness.[50−52] When the chiral carboxylic acid, D-mandelic acid, was added to solutions of **3** in 90% H_2O/DMSO, a CD spectrum was obtained with a negative ellipticity characteristic of the absorption spectra for this polymer as shown in Figure 4. In addition, the same experiment performed in DMSO resulted in no observed change in ellipticity. The CD spectrum of D-mandelic acid in 90% H_2O/DMSO without **3** also resulted in a spectrum with no change in molar ellipticity. The appearance of a negative molar ellipticity from solutions of **3** in 90% H_2O/DMSO with D-mandelic acid but no change in molar ellipticity from DMSO solutions is consistent with a helical conformation of **3** in 90% H_2O/DMSO. Chiral guest experiments were also conducted, but no change in ellipticity could be observed.[27]

Conclusions

The solution conformations of facially amphiphilic polymers based on *m*-PPE backbones were studied. Those with alkyl substituents clearly form extended structures even in 90% H_2O/DMSO solution,[31,32] while polymers without alkyl side chains appear to adopt alternative conformations with spectroscopic features similar to helical structures reported in the literature.[29] CD spectroscopy in the presence of a chiral carboxylic acid additive showed a signal consistent with a helical structure. Although intermolecular self-assembly into cylindrical or other structures cannot be entirely ruled out, these other structures are not consistent with the UV−vis spectra. The benzyl ether function may not produce the most stable helical conformations, according to Moore, and this might also influence the results discussed here. However, it can be safely concluded that *m*-PPEs without alkyl groups adopt different conformations and structures in solution than those with alkyl groups. Polymers with significantly higher molecular weights should eliminate the influence of small chains on the titration curves and are a future synthetic target. This is the initial report of polydisperse phenylene ethynylenes folding in solution toward helical structures and demonstrates some of the difficulties that will be encountered during these studies. The ability to control molecular conformation by side chain decoration of the backbone with polar and nonpolar groups leads to some interesting opportunities.

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Supporting Information Available: Fluorescence spectra of polymer **1** and polymer **3** in $CHCl_3$, DMSO, and 90% H_2O/DMSO. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added in Proof: During publication of this manuscript, we contacted other research groups working on related systems. Moore and coworkers have studied polymeric versions of their oligomers (personal communication). Hecht and coworkers published a paper in December describing the covalent capture of helical folds based on ethylene glycol non-ionic m-PPE's (*Angew. Chem. Int. Ed.* **2003**, *42*, 6021−6024). Schanze and coworkers are studying an anionic polyelectrolyte system with helical conformations (submitted for publication).

References and Notes

(1) Friedman, R. A.; Honig, B. *Biophys. J.* **1995**, *69*, 1528−1535.
(2) Delnoye, D. A. P.; Sijbesma, R. P.; Vekemans, J.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118*, 8717−8718.
(3) Brunsveld, L.; Zhang, H.; Glasbeek, M.; Vekemans, J.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 6175−6182.
(4) Bielawski, C.; Chen, Y. S.; Zhang, P.; Prest, P. J.; Moore, J. S. *Chem. Commun.* **1998**, 1313−1314.
(5) Yagi, S.; Sakai, N.; Yamada, R.; Takahashi, H.; Mizutani, T.; Takagishi, T.; Kitagawa, S.; Ogoshi, H. *Chem. Commun.* **1999**, 911−912.
(6) Prince, R. B.; Okada, T.; Moore, J. S. *Angew., Chem., Int. Ed.* **1999**, *38*, 233−236.
(7) Ben-Naim, A. *J. Chem. Phys.* **1971**, *54*, 1387−1404.
(8) Lahiri, S.; Thompson, J. L.; Moore, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 11315−11319.
(9) Nelson, J. C.; Saven, J. G.; Moore, J. S.; Wolynes, P. G. *Science* **1997**, *277*, 1793−1796.
(10) Cubberley, M. S.; Iverson, B. L. *J. Am. Chem. Soc.* **2001**, *123*, 7560−7563.
(11) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525−5534.
(12) Chan, H. S.; Dill, K. A. *Macromolecules* **1989**, *22*, 4559−4573.
(13) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(14) Gellman, S. H. *Acc. Chem. Res.* **1998**, *31*, 173−180.
(15) Iverson, B. *Nature (London)* **1997**, *385*, 114.
(16) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893−4011.
(17) Smith, M. D.; Claridge, T. D. W.; Tranter, G. E.; Sansom, M. S. P.; Fleet, G. W. J. *Chem. Commun.* **1998**, 2041−2042.
(18) Seebach, D.; Matthers, J. L. *Chem. Commun.* **1997**, 2015−2022.
(19) Cheng, R. P.; Gellman, S. H.; DeGrado, W. F. *Chem. Rev.* **2001**, *101*, 3219−3232.
(20) Kirshenbaum, K.; Barron, A. E.; Goldsmith, R. A.; Armand, P.; Bradley, E. K.; Truong, K. T. V.; Dill, K. A.; Cohen, F. E.; Zuckermann, R. N. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, *95*, 4303−4308.
(21) Jiang, H.; Leger, J.-M.; Huc, I. *J. Am. Chem. Soc.* **2003**, *125*, 3448−3449.
(22) Hamuro, Y.; Geib, S. J.; Hamilton, A. D. *J. Am. Chem. Soc.* **1997**, *119*, 10587−10593.
(23) Hamuro, Y.; Geib, S. J.; Hamilton, A. D. *J. Am. Chem. Soc.* **1996**, *118*, 7529−7541.

(24) Berl, V.; Huc, I.; Khoury, R. G.; Krische, M. J.; Lehn, J.-M. *Nature (London)* **2000**, *407*, 720−723.
(25) Berl, V.; Huc, I.; Khoury, R. G.; Lehn, J.-M. *Chem.−Eur. J.* **2001**, *7*, 2810−2820.
(26) Hill, D. J.; Moore, J. S. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5053−5057.
(27) Prince, R. B.; Barnes, S. A.; Moore, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 2758−2762.
(28) Cary, J. M.; Moore, J. S. *Org. Lett.* **2002**, *4*, 4663−4666.
(29) Prince, R. B.; Saven, J. G.; Wolynes, P. G.; Moore, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 3114−3121.
(30) Arnt, L.; Tew, G. N. *J. Am. Chem. Soc.* **2002**, *124*, 7664−7665.
(31) Arnt, L.; Tew, G. N. *Langmuir* **2003**, *19*, 2404−2408.
(32) Arnt, L.; Kim, T.; Strey, H.; Tew, G. N., manuscript in preparation.
(33) Kubel, C.; Mio, M. J.; Moore, J. S.; Martin, D. C. *J. Am. Chem. Soc.* **2002**, *124*, 8605−8610.
(34) Prest, P.-J.; Prince, R. B.; Moore, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 5933−5939.
(35) McQuade, D. T.; Kim, J.; Swager, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 5885−5886.
(36) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605−1644.
(37) Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, U. H. F. *Macromolecules* **1998**, *31*, 8655−8659.
(38) Kim, J.; Swager, T. M. *Nature (London)* **2001**, *411*, 1030−1034.
(39) See Supporting Information.
(40) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970.
(41) Tompa, H. *Trans. Faraday Soc.* **1950**, *46*, 970.
(42) Rulkens, R.; Wegner, G.; Thurn-Albrecht, T. *Langmuir* **1999**, *15*, 4022−4025.
(43) Bockstaller, M.; Kohler, W.; Wegner, G.; Vlassopoulos, D.; Fytas, G. *Macromolecules* **2001**, *34*, 6359−6366.
(44) Mays, J. W. In *Modern Methods of Polymer Characterizations*; Barth, H. G., Mays, J. W., Eds.; John Wiley and Sons: New York, 1991.
(45) Kloppenburg, L.; Jones, D.; Claridge, J. B.; zur Loye, H.-C.; Bunz, U. H. F. *Macromolecules* **1999**, *32*, 4460−4463.
(46) Kloppenburg, L.; Jones, D.; Bunz, U. H. F. *Macromolecules* **1999**, *32*, 4194−4203.
(47) Vanhee, S.; Rulkens, R.; Lehmann, U.; Rosenauer, C.; Schulze, M.; Kohler, W.; Wegner, G. *Macromolecules* **1996**, *29*, 5136−5142.
(48) Choudry, U. H.; Marshall, A. R.; Bunz, U. H. F. *Macromolecules* **2003**, *36*, 1424−1425.
(49) Cornelissen, J.; Peeters, E.; Janssen, R. A. J.; Meijer, E. W. *Acta Polym.* **1998**, *49*, 471−476.
(50) Maeda, K.; Okada, S.; Yashima, E.; Okamoto, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3180−3189.
(51) Lermo, E. R.; Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Meijer, E. W. *Chem. Commun.* **1999**, 791−792.
(52) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860−1866.

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