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Hexagonal Packing of Oligo(*m*-phenylene ethynylene)s in the Solid State: Helical Nanotubules

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The design and synthesis of nonbiological oligomers with ordered solution conformations has come to the forefront of organic chemical research.[1,2] Our group has examined a variety of oligo(*m*-phenylene ethynylene)s and found a cooperative folding transition in polar solvents from a random coil to a helical conformation.[3,4] Recently, our interests have broadened to include analyzing the structure of these oligomers in the solid state, as well.[5] Building on the molecules' ability to fold into compact helices, a nanotubular arrangement can be imagined. Such a structure would be interesting not just for its uniqueness[6] or ability to organize spontaneously[7,8] but also for its possible uses as an organic host solid[9] and template for nano-organization.[10] Solid-state characterization of these oligomers poses many challenges, as they are poorly ordered, waxy substances at room temperature, making single crystal generation difficult. Thus, to investigate their solid-state packing, we performed small- and wide-angle X-ray diffraction (SAXD and WAXD) studies on two series of discrete oligomers. Previously accrued data only revealed an extended lamellar ("boardlike") packing motif for oligomer series **1**.[5] Although a hexagonal tubular phase was predicted, no evidence for this type of organization was found in this initial study. Herein, we report that a slight modification of the oligomeric backbone (**1**, R = H to **2**, R = CH$_3$) leads to a hexagonal arrangement of helical columns in the solid state. We propose that hexagonal packing is the kinetically preferred phase for those oligomers that form stable helical conformations in solution.[11]

The syntheses of oligomer series **1** (n = 8, 10, 12, 14, 16, 18) and **2** (n = 4, 6, 12) have been reported.[4,12] Other members of series **2** (n = 8, 10, 14, 16, 18) were prepared in a similar fashion.[13] Previously, X-ray diffraction samples of series **1** were obtained by slow cooling from the melt. This method was not deemed viable for series **2**, as several of its longer members ($n \geq 12$) decompose prior to melting. As a result, a new sample preparation method was developed wherein oligomers were dissolved in a small amount of solvent (CH$_2$Cl$_2$), drawn up into capillaries, and left to solidify as evaporation took place.

The SAXD and WAXD patterns of oligomer series **1** were *not* dependent on the sample preparation method. Samples of **2** that could be prepared from the melt showed lamellar phases similar to those of **1**. However, when prepared by the solvent evaporation method, the *endo*-methyl-substituted oligomers **2** ($n \geq 10$) exhibited a chain-length independent long-spacing (25−26 Å), in great contrast to the lamellar phase of **1**, in which the long-spacing was linearly correlated to chain length (Figure 1).[14] A possibility consistent with this observation would be that those oligomers in series **2** adopt the hexagonal arrangement in Figure 1. One could imagine the helices stacking atop one another to make columns that laterally assemble in a hexagonal fashion.[15,16]

Many facets of this diffraction data support the possibility of helical stacks organized in a hexagonal fashion. Several of the SAXD and WAXD patterns for series **2** manifested obvious 6-fold symmetry (Figure 2, left). Such patterns result from macroscopic order which spontaneously arose in the preparation of many samples of **2**. This was the only type of macroscopic orientation observed. The observed X-ray patterns designate a radially oriented array of helical columns where column axes are perpendicular to the capillary axis and the hexagonal 100 planes run parallel to the capillary axis (Figure 2, right). Further WAXD data taken without rotation scanning confirm this radial symmetry (see Supporting Information). Reflections seen in the aligned WAXD data specify that the Bragg planes corresponding to the 3.6 Å *d*-spacing ($\pi-\pi$ stacking) are perpendicular to those Bragg planes that align parallel to the capillary axis.

For all oligomers **2** $n \geq 10$, the WAXD profiles are very similar (Figure 3). The small-angle reflections correspond to a *d*-spacing ratio of $1{:}1/\sqrt{3}{:}0.5{:}1/\sqrt{7}$, and thus index to a hexagonal lattice. Such reflections are not observed in **2** (n = 4 and 8), which are too short to fold into a stable helix in solution. The tetramer and octamer exhibit lamellar packing akin to **1**, even when prepared from solution. In addition, preliminary electron microscopy data has been acquired for **2** (n = 18).[17]

Oligomers **2** n = 6 and n = 10 are worthy of comment here. In SAXD measurements, the decamer displays peaks that correspond to *both* lamellar and hexagonal packing.[18] This observa-

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(13) All products were characterized by ^{1}H NMR and mass spectrometry (FAB or MALDI). Purity was assessed by HPLC and GPC. As in our previous studies with these oligomers, the UV−vis absorption spectra and fluorescence emission spectra were solvent-dependent for all molecules except for sequences shorter than 10 units. Such oligomers are too short to solvophobically collapse into stable helical conformations.

(14) Samples were stable at ambient temperature and pressure for at least 4 months. No change in X-ray patterns was observed after evacuation. Thus, we rule out a lyotropic phase.

(15) Hexagonal packing in such a way would explain why the oligomer long-spacing no longer depends on chain-length. Precedence for this type of organization can be found in the literature.[16] However, in these cases, very little internal space remains. In the case of series **2**, an internal tube diameter of approximately 7 Å is generated.

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(17) While the hydrogen-substituted octadecamer **1** (n = 18) has yet to be imaged due to the thickness of crystals, selected area electron diffraction (SAED) patterns of the methyl-substituted analogue **2** (n = 18) support the conclusion of hexagonal packing with lattice spacings of ~30 Å. Lattice fringes of different crystallographic zones, including the ~26 Å (100) and the ~15.5 Å (110) spacings, were observed in high-resolution transmission electron microscopy (HR-TEM) and are consistent with the proposed structure.

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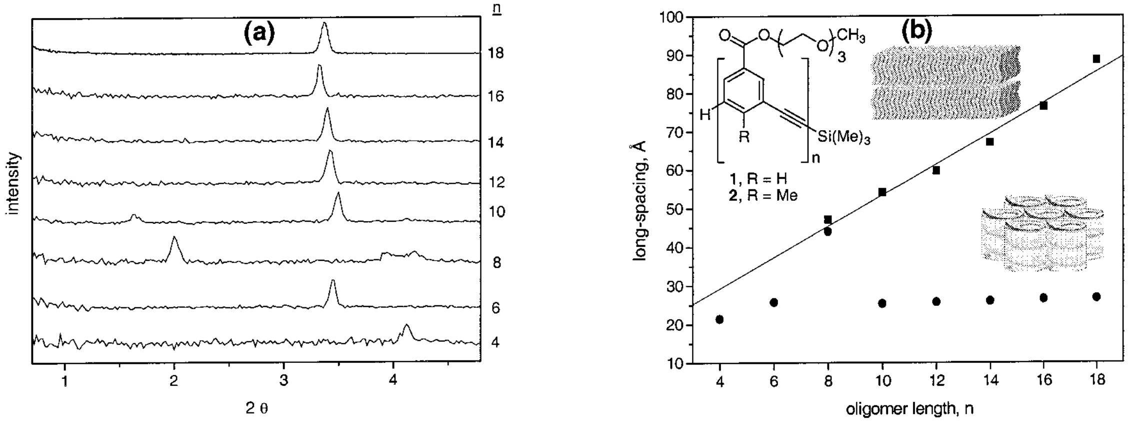

Figure 1. (a) SAXD profiles for series **2** at room temperature. (b) Plot of long-spacings versus oligomer length for two oligo(*m*-phenylene ethynylene) series as observed in SAXD measurements. Series **1** (prepared from the melt) packs in a lamellar arrangement(■, pictured top), and thus the long spacings depend linearly on chain length.[5] In contrast, series **2** (prepared from solvent evaporation) exhibits long spacings that are independent of chain-length (n ≥ 10), suggesting the possibility of helical columns (●, pictured bottom).

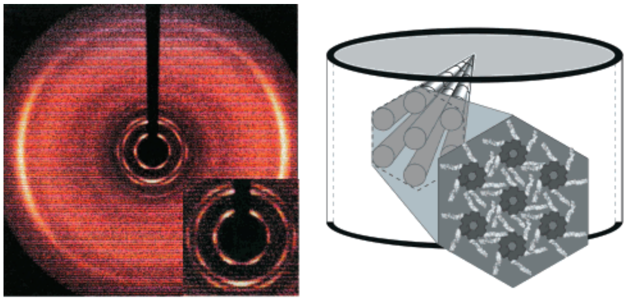

Figure 2. (Left) Detail of a WAXD pattern for **2** ($n = 14$) prepared by the solvent evaporation method. The capillary axis is vertical. The pattern is demonstrative of a macroscopically oriented radial packing arrangement of the helical columns. The inset is an expanded view of the small-angle region. (Right) A schematic diagram consistent with the observed macroscopic radial packing arrangement of oligo(*m*-phenylene ethynylene) series **2** in the capillary tube.

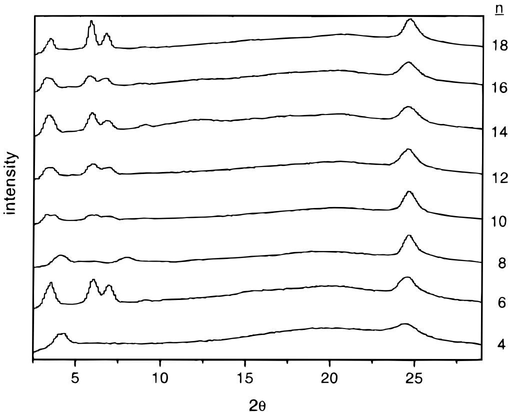

Figure 3. WAXD profiles for series **2** at room temperature. Profiles for $n = 6$, 10, 12, 14, 16, and 18 index to a hexagonal lattice; $a = 30$ Å.

tion is not entirely unexpected. Solution-phase data indicates that the decamer forms a less stable helical conformation than longer members of series **2**. Hence the oligomer's inability to adopt a single solid-state organizational motif.[19] In contrast, although the hexamer is too short to fold into a stable helix in solution, it is clearly packing hexagonally. This oligomer can adopt an all-cisoid, planar conformation much like those of phenylacetylene macrocycles.[20] Such structures have been shown to self-assemble into columnar liquid crystals.

We have previously used UV−vis absorption spectroscopy to study the conformation of phenylacetylene oligomers in solution.[3,4,11,12,21] Accordingly, we wanted to compare the UV spectra of solution-cast thin films to spectra in dilute solution. When **2** is dissolved in $CHCl_3$, its spectrum ($n = 10$ and 18) shows two maxima at 295 and 315 nm. In such solvent, the oligomers are in random coil conformations, where cisoid and transoid torsional states are nearly equally populated. When **2** is in CH_3CN, where the conformation is thought to be predominantly cisoid (helical), the spectrum shows a significantly decreased absorbance in the 315 nm band relative to the 295 nm band. Solid-state spectra taken on thin films of **2** ($n = 10$ and 18) cast from CH_2Cl_2 show broad bands, but the two diagnostic maxima are visible. The ratio of these peak intensities is similar to those taken in CH_3CN solutions.

We have demonstrated that the introduction of methyl groups into the *endo*- positions of oligo(*m*-phenylene ethynylene)s results in the formation of helical nanotubules in the solid state. On the basis of SAXD and WAXD data, this solid-state packing is observed for those sequences that have the most stable helical conformations in solution (see Supporting Information). It has also been established that these molecules spontaneously acquire radial macroscopic orientation, where the helical columns are perpendicular to the capillary axis. This structure has possible applications as an organic host solid and use as a template for nano-organization. Extensions of these findings to other oligo(*m*-phenylene ethynylene) systems including polydisperse materials are presently underway and will be reported in due course.

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Supporting Information Available: Synthesis of **2** ($n = 8$, 10, 14, 16, 18), melting point data, X-ray sample preparation details, additional WAXD and SAXD data, and solid-state UV−vis spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Rigorous steps were taken to ensure these signals were not due to a sample impurity or instrumental artifacts.

(19) The observed hexagonal packing is most likely metastable since those oligomers of **2** prepared from the melt form lamellar phases.

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