Helical Organization of *m*-Linked Rigid Polymers with Pendant Flexible Dendrons

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The spontaneous formation of helical structures by self-assembly of amphiphilic molecules is of great interest in areas ranging from biomimetic to synthetic systems.[1] Helical assembly has been achieved by a variety of strategies including intramolecular hydrogen bonding,[2–4] solvophobic effects,[5] and metal–ligand interactions.[6] For example, discrete oligomer chains based on the connection of aromatic moieties in a *meta* geometry can fold through specific intramolecular interactions into a helical object which, in turn, undergoes self-assembly into a columnar entity.[5–8] Relatively strong, directional interactions, such as complexation between conformationally restricted bent shaped ligands and transition metals that adopt a linear coordination geometry, can also give rise to extended polymeric chains with a helical secondary structure.[9,10]

A previous publication from our laboratory has demonstrated that the organized structure of coordination polymers in the solid state appears to be dependent on the size of the counterionic guest.[11] As the size of the counteranion increases, the organized structure changes, from a 2-D hexagonal columnar structure based on either helical chains or dimeric cycles to a lamellar structure based on linear chains. This observation stimulated us to envisage that the secondary structure of polymer chains based on the connection of aromatic moieties in a *meta* geometry can be controlled from a folded helical conformation to an unfolded conformation by attaching chemically dissimilar, flexible dendrons as a side groups. As the cross-sectional area of the dendritic wedge of the polymer increases, greater steric repulsion between adjacent dendritic wedges could possibly cause a transformation into a helical conformation in order to relieve the repulsive forces. This implies that introduction of bulky side groups into a polymer based on a *meta* geometry can give rise to the formation of a folded secondary structure.

In this communication, conformationally flexible, *m*-linked rigid monomers containing a flexible side group have been synthesized and polymerized with with 4,4′-bis(bromomethyl)biphenyl to yield *m*-linked aromatic polymers (Scheme 1). Notably, the secondary structure of the resulting polymers appears to be dependent on the molecular structure of the side group in the solid state. Polymer **1a** based on a linear side chain appears to self-organize into a lamellar structure based on an unfolded conformation. In great contrast, polymer **1b** based on a bulky dendritic side group self-assembles into a 2-D tetragonal structure based on a helical conformation (Figure 1). In addition, the polymers containing a dendritic side group are able to wrap single-walled carbon nanotubes (SWNT) in THF solution by forming helical structure via host–guest $\pi-\pi$ interactions.

The aromatic polymers that form these aggregates consist of a *m*-linked rigid backbone and flexible aliphatic chains (Figure 1). The precursors of the monomers were prepared from the etherification of the corresponding tosyl-terminated ether with 3,5-dibromophenol in the presence of potassium carbonate.[11,12] The monomers were prepared from the Suzuki coupling reaction of the corresponding precursor with 4-(*tert*-butyldimethylsilyoxy)biphenylboronic acid. Polymerization of the resulting monomers was performed with 4,4′-bis(bromomethyl)biphenyl via etherification to yield the corresponding polymers. Number-average molecular weights (M_n) of **1a** and **1b** were observed to be 79 000 and 78 000 Da, respectively, with polydispersity indexes (PDI) of about 1.7 by gel permeation chromatography GPC, with reference to polystyrene standards.

The polymers appeared to be birefringent solids that melt into isotropic liquid at 179 and 160 °C for **1a** and **1b**, respectively (Figure 2a). Small-angle X-ray scattering (SAXS) measurements of **1a** showed two sharp reflections corresponding to a 1-D lamellar structure with a lattice dimension of 5.5 nm (Figure 2b). The lamellar structure with this dimension indicates that the rigid polymer chain of **1a** adopts an unfolded zigzag conformation. In contrast to that of **1a**, polymer **1b** based on a bulky dendritic side group showed two sharp reflections with a spacing ratio of $1:\sqrt{2}$ (Figure 2b), indicative of an unusual 2-D tetragonal columnar structure (*P*4*mm* space group) with a lattice parameter of 3.6 nm.[13] This phase identification was further confirmed by transmission electron microscopy (TEM). The TEM images stained with RuO_4 and ED pattern showed a tetragonal array of dark spots in a matrix of light aliphatic segments (Figure 2c,d). The interdomain distance appeared to be approximately 3.5 nm, which is consistent with that obtained from SAXS. These results suggest that the polymer chains of **1b** adopt a helical conformation that self-organizes into a 2-D tetragonal lattice. The formation of a helical structure is further supported by TEM which showed that the thickness of a dark aromatic domain appeared to be approximately 2 nm, corresponding to the thickness of an aromatic helical structure (2.2 nm by CPK). Compared to **1a**, the bulky dendritic geometry of the flexible segments relative to a linear chain is likely to prohibit the 2D growth of a self-assembled structure. Instead, the polymer chains containing bulky dendrons are strongly driven to aggregate in one dimension with a helical packing through microphase separation between the rigid aromatic core and flexible dendron segments and $\pi-\pi$ stacking interactions between aromatic units in order to relieve steric repulsions between bulky dendrons.

The formation of a helical structure motivated us to investigate if the *m*-linked aromatic polymers wrap SWNTs in solution through $\pi-\pi$ interactions between aromatic units.[14] With this consideration in mind, wrapping capability of aromatic chains with **1b** was evaluated by using fluorescence spectroscopy. SWNTs were observed to be solubilized in THF by mixing with **1b** along with sonication (solubility of about 0.5 mg/mL).

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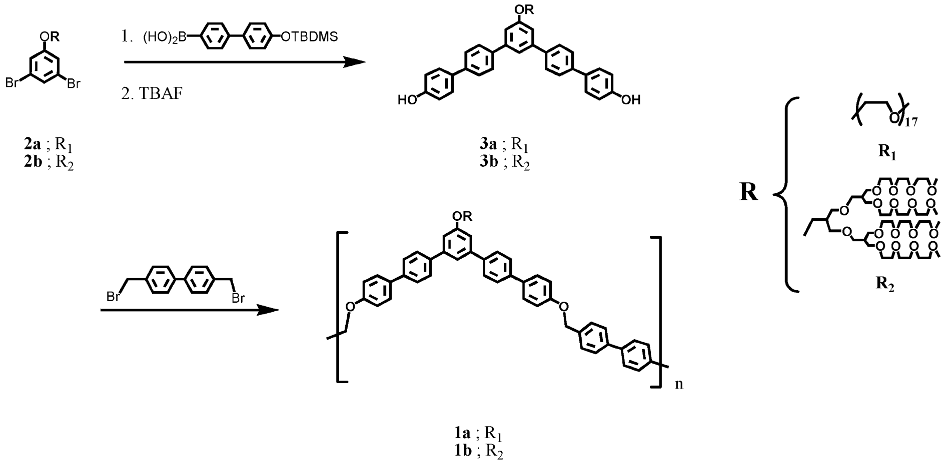
Scheme 1. Synthesis of *m*-Linked Rigid Polymers 1a and 1b



The emission spectrum of the THF solution, in the absence of SWNTs, displayed a strong fluorescence with a maximum at 370 nm (Figure 3a).[15] In great contrast, the fluorescence intensity of the solution containing SWNTs was significantly suppressed because of fluorescence quenching, indicating that they are effectively wrapped by conformationally flexible aromatic chains through hydrophobic interactions and $\pi-\pi$ stacking interactions.[14a,16] The wrapping of SWNTs by polymer chains was further supported by TEM (Figure 3b). The

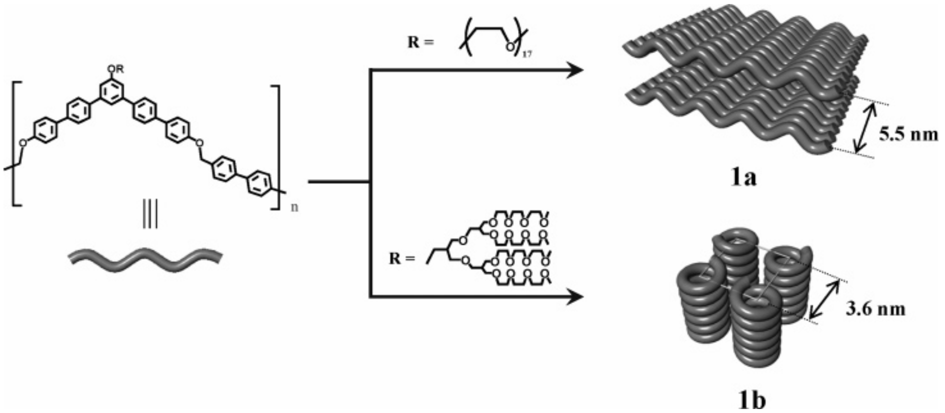


Figure 1. Schematic representation for the formation of lamellar of **1a** and tetragonal columnar of **1b**.

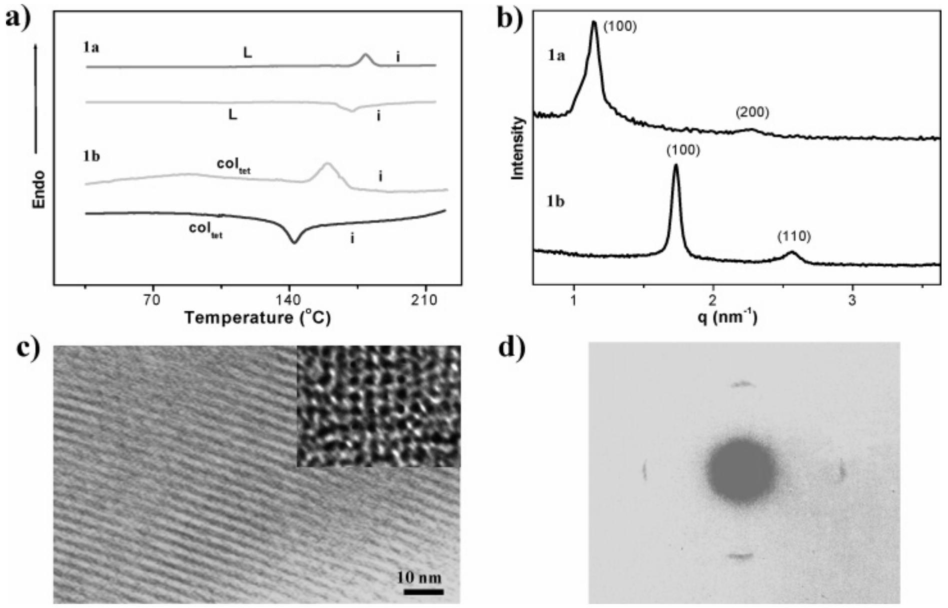


Figure 2. (a) DSC traces (10 °C/min) recorded during the heating and cooling scans of polymers **1a** and **1b**, (b) small-angle X-ray diffraction patterns measured at room temperature plotted against q (= $4\pi \sin(\theta/\lambda)$) for **1a** and **1b**, and (c) TEM images of ultramicrotomed films of polymer **1b** stained with RuO_4 revealing columnar array of alternating light-colored dendritic layer and dark aromatic layers. The inset image at perpendicular beam incidence shows a tetragonally ordered array of aromatic core. (d) Small-angle electron diffraction pattern of **1b** at perpendicular beam incidence shows the tetragonal morphology.

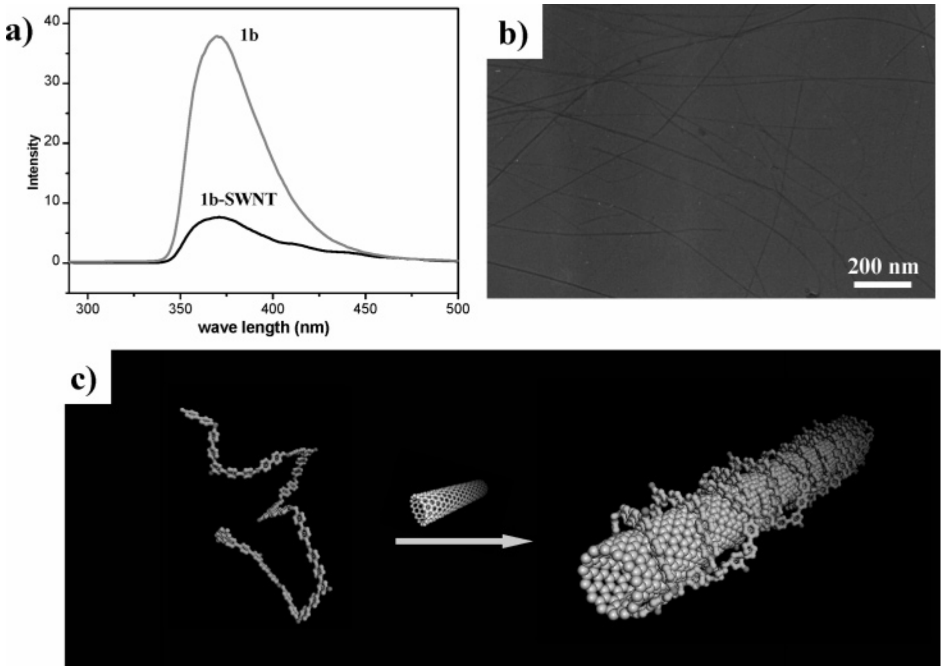


Figure 3. (a) Fluorescence spectra of the THF solution of **1b** and of **1b**-SWNT (excitation wavelength: 280 nm), (b) TEM image of the THF solution of **1b** containing SWNTs, and (c) schematic representation of the wrapping of SWNTs by polymer chains.

image shows well-separated long cylindrical objects with a uniform diameter of about 5 nm that is approximately correspond to a helical columnar dimension. These results together with significant band broadening in the ^{1}H NMR spectrum[14c] suggest that the aromatic polymer chains wrap around SWNTs by forming a helical structure in order to maximize $\pi-\pi$ interactions between aromatic polymer chains and carbon nanotubes (Figure 3c).

In conclusion, we have demonstrated that the amphiphilic *m*-linked rigid polymer based on an oligo(ethylene oxide) chain self-assembles into a lamellar structure based on an unfolded conformation. In contrast, the polymer based on a bulky dendritic chain adopts a helical conformation that self-organizes into a tetragonal columnar structure. Interestingly, the polymer based on a dendritic side group can encapsulate SWNT by wrapping with helical conformation. The results suggest that this class of self-assembling system may allow the design of well-defined helical tubules with desired functions.

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Supporting Information Available: Detailed synthetic procedures, characterization, GPC, and NMR. This material is available free of charge via the Internet at http//pubs.acs.org.

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