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 control from a 3D to a 2D growth of a self-assembled structure. Instead, 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:√2 (Figure 2b), indicative of an unusual 2-D tetragonal columnar structure (P4mm 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 RuO4 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 π−π 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 π−π 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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The emission spectrum of the THF solution, in the absence of SWNTs, displayed a strong fluorescence with a maximum at 370 nm (Figure 3a). 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. The wrapping of SWNTs by polymer chains was further supported by TEM (Figure 3b). The

![Scheme 1. Synthesis of \( m \)-Linked Rigid Polymers 1a and 1b]

![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 \( q = 4\pi \sin(\theta/2) \) for 1a and 1b, and (c) TEM images of ultramicrotomed films of polymer 1b stained with RuO4 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.]

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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 SWNTs and carbon nanotubes (Figure 3c).

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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.

References and Notes


(15) It should be noted that this polymer exhibits a lack of aggregation behavior in THF solution.


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