

Self-assembly of Amphiphilic Linear Diblock Rod-Coil Molecules by Hydrogen Bond and π - π Stacking Interactions^{*}

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Abstract Aromatic amphiphilic molecules (**1**) consisting of three biphenyl groups linked together with ether bonds as a rigid rod segment and poly(ethylene oxide) with the number of repeating units of 17 as a coil segment were synthesized, and their self-assembly behavior in the bulk state and aqueous solution was investigated. In bulk, molecules **1** self-assembled into 1-D lamellar structure in the solid state or smectic A phase in the liquid crystalline phase *via* the cooperative effects of π - π stacking, micro-phase separation and hydrogen bond interactions. In dilute aqueous solutions, molecules **1** were observed to self-assemble into cylindrical micelles owned uniform diameter and length of hundreds of nanometers.

Keywords: Rod-coil; Self-assembly; Smectic A phase; Cylindrical micelles; SAXS.

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INTRODUCTION

The supramolecular self-assembly of arene-based rod-coil molecules with strong, well defined π - π stacking interactions is a topic of great importance because it opens a new way to regulate both the molecular assembly and the optoelectronic properties of these materials^[1–5]. Oligo-ether can act as a kind of excellent flexible chain because it exhibits high thermal/chemical stability and excellent hydrophile^[6–8]. Amphiphilic arene-based rod-coil molecules with oligo-ether chains have a strong tendency to self-organize into a variety of supramolecular structures in nano-scale dimensions through tuning hydrophobic and hydrophilic effects, electrostatic interactions, hydrogen bonding, micro phase segregation and shape effects *etc.*^[9–13]. The aggregation of such rod-coil block molecules has generated a number of nanoscale morphologies, such as lamellar, hexagonal columnar, body-centered tetragonal, bicontinuous cubic, spherical, cylindrical, vesicular, micro-porous structures and so on in bulk and aqueous solution^[14–18].

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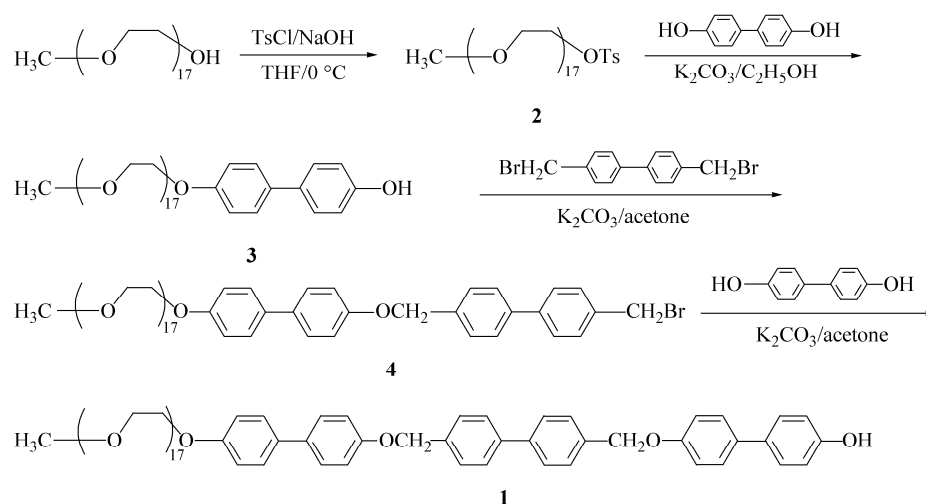
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We have recently demonstrated that the self-assembly of rod-coil molecules is affected by the length of lateral chain in the center of the rod^[19, 20], the shape of rigid rod^[21], the join sequence of rod segments^[22], polarity of lateral chain in the center of the rod *etc.*^[23]. We have found if a chemically distinct hydrophilic lateral chain such as carboxyl group is attached to the middle of a rod segment which leads to various ordered supramolecular nanostructures because of the hydrogen bonding interaction of carboxyl groups^[23]. Inspired by the experiment results, when phenolic hydroxyl group is introduced into the end of rod segment, we expect that the hydrogen bonding combining π - π stacking interactions may bring about the formation of a novel nanostructure.

With this idea in mind, we have synthesized a novel linear diblock rod-coil compound **1** containing phenolic hydroxyl group at the end of rod (Scheme 1). We discussed the self-assembly behavior of **1** in the bulk state and in aqueous medium by means of optical polarized microscopy, differential scanning calorimetry (DSC), powder X-ray diffraction (XRD), dynamic light scattering (DLS) and transmission electron microscopy (TEM).



Scheme 1 Synthetic route of **1**

EXPERIMENTAL

Materials

Poly(ethylene glycol) methyl ether ($M_w = 750$), toluene-*p*-sulfonyl chloride (TsCl, 98%), 4,4'-dihydroxybiphenyl (all from J&K CHEMICAL LTD.) and the conventional reagents were used as received.

Synthesis

Synthesis of compound **2**

A mixture of poly(ethylene glycol) methyl ether ($M_w = 750$) (15 g, 20 mmol) dissolved in dry tetrahydrofuran (12 mL) and NaOH (0.96 g, 24 mmol) dissolved in water (9.5 g) was put into a two-neck flask. Toluene-*p*-sulfonyl chloride (TsCl, 4.58 g, 24 mmol) dissolved in dry tetrahydrofuran (50 mL) was added by drops for 4 h at 0 °C. The reaction mixture was further stirred for 4 h at 0 °C. The resulting solution was dissolved in ice water (20 mL) and extracted with methylene chloride. The organic solution was dried (MgSO_4) and filtered. The solvent was removed in a rotary evaporator and the crude product was purified by column chromatography on silica gel using CH_2Cl_2 , CH_2Cl_2 :MeOH (20:1 *V/V*) as eluent to yield 14.1 g of colorless liquid (78%). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 7.79 (d, 2Ar-H, *o* to SO_3 , $J = 8.2\text{ Hz}$), 7.33 (d, 2Ar-H, *o* to CH_3 , $J = 8.2\text{ Hz}$), 4.14 (t, 2H, $\text{OCH}_2\text{CH}_2\text{OSO}_2$), 3.52–3.68 (m, 66H, $-\text{OCH}_2\text{CH}_2\text{O}-$ and $\text{OCH}_2\text{CH}_2\text{OSO}_2$), 3.24 (s, 3H, OCH_3), 2.43 (s, 3H, CH_3Phenyl).

Synthesis of compound 3

Excess K_2CO_3 and 4,4'-biphenol (9.0 g, 48.4 mmol) were dissolved in absolute ethyl alcohol (120 mL). Compound **2** (11 g, 12.1 mmol) dissolved in absolute EtOH (50 mL) was added by drops into the above mixture for 7 h under reflux condition. The mixture was further refluxed for 15 h. The solvent was removed in a rotary evaporator. Water, a small amount of dilute H_2SO_4 were added into the resulting mixture, extracted with ethyl acetate. The ethyl acetate solution was neutralized with Na_2CO_3 , dried over anhydrous magnesium sulfate and filtered. After the solvent was removed in a rotary evaporator, the crude product was purified by silica gel chromatography to yield 12.35 g of a yellow ropy liquid (85%). ^1H -NMR (300 MHz, $CDCl_3$, δ) 7.37–7.47 (m, 4Ar–H, *m* to phenyl–OH, *m* to CH_2O phenyl), 6.88–6.96 (m, 4Ar–H, *o* to phenyl–OH, *o* to CH_2O phenyl), 6.65 (m, 1H, OH), 4.15 (t, 2H, $phenylOCH_2CH_2O$, $J = 5.0$ Hz), 3.87 (t, 2H, $phenylOCH_2CH_2O$, $J = 5.0$ Hz), 3.54–3.74 (m, 64H, $-OCH_2CH_2O-$), 3.37 (s, 3H, OCH_3).

Synthesis of compound 4

Excess K_2CO_3 (2.33 g, 16.8 mmol), NaI (0.5 g, 3.35 mmol) and 4,4'-bis(bromomethyl)biphenyl (5.7 g, 16.8 mmol) were dissolved in acetone (85 mL). Compound **3** (3.15 g, 3.35 mmol) was added by drops into the above mixture for 2 h under reflux condition. The mixture was further refluxed for 22 h, filtered and concentrated by evaporation, then separated by chromatography on silica gel (CH_2Cl_2 , EA, $CH_2Cl_2:CH_3OH = 20:1$, V/V , as eluent). The desired compound was separated as the most polar fraction to yield 3.40 g of a wax-like white solid (84%). ^1H -NMR (300 MHz, $CDCl_3$, δ) 7.47–7.62 (m, 12Ar–H, *o* to OCH_2 phenyl, *m* to OCH_2 phenyl, *o* to CH_2Br , *m* to CH_2Br , *m* to CH_2O phenyl and *m* to $phenylOCH_2CH_2O$), 6.96–7.04 (dd, 4Ar–H, *o* to CH_2O phenyl, *o* to $phenylOCH_2CH_2O$, $J = 8.5$ Hz), 5.14 (s, 2H, OCH_2 phenyl), 4.55 (s, 2H, CH_2Br), 4.16 (t, 2H, $phenylOCH_2CH_2O$), 3.87 (t, 2H, $phenylOCH_2CH_2O$), 3.55–3.72 (m, 64H, $-OCH_2CH_2O-$), 3.37 (s, 3H, OCH_3).

Synthesis of rod-coil compound 1

Compound **4** (3.70 g, 3.1 mmol), 4,4'-biphenol (2.52 g, 12.4 mmol) and excess K_2CO_3 were dissolved in acetone (100 mL). The mixture was refluxed for 30 h and then cooled to room temperature. After filtered, the solvent was removed and the crude product was purified by chromatography on silica gel (EA, $CH_2Cl_2:CH_3OH = 10:1$, V/V , as eluent). The desired compound was separated as the most polar fraction to yield 3.30 g of a wax-like light yellow solid (81%). ^1H -NMR (300 MHz, $CDCl_3$, δ) 7.48–7.62 (m, 16Ar–H, *o* to OCH_2 phenyl, *m* to OCH_2 phenyl, *m* to CH_2O phenyl, *m* to phenylOH, *m* to $phenylOCH_2CH_2O$), 6.88–7.06 (m, 8Ar–H, *o* to CH_2O phenyl, *o* to phenylOH, *o* to $phenylOCH_2CH_2O$), 5.45 (m, 1H, OH), 5.15 (s, 2H, OCH_2 phenyl), 4.16 (t, 2H, $phenylOCH_2CH_2O$), 3.88 (t, 2H, $phenylOCH_2CH_2O$), 3.55–3.73 (m, 64H, $-OCH_2CH_2O-$), 3.38 (s, 3H, OCH_3), MALDI-TOF-MS m/z ($M+Na$)⁺ 1335.7, ($M+K$)⁺ 1351.8.

Characterization Techniques

The purity of the products was checked by column chromatography (silica gel 100–200). ^1H -NMR spectra were recorded from $CDCl_3$ solutions on a Bruker AM 300 spectrometer. MALDI-TOF-MS was performed on a perceptive Biosystems Voyager-DE STR using 2-cyano-3-(4-hydroxyphenyl) acrylic acid (CHCA) as matrix. A Perkin Elmer Pyris Diamond differential scanning calorimeter was used to determine the thermal transitions, which were reported as the maxima and minima of their endothermic or exothermic peaks, the heating and cooling rates were controlled to be 10 K/min. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 3C2 X-ray beam line at Pohang Accelerator Laboratory, Korea. The scattering vector q is defined as $q = 4\pi/\lambda \sin\theta$, where the scattering angle is 2θ , and the d -spacing (d) is given by $2\pi/q$. A Nikon Optiphot 2-pol optical polarized microscope, equipped with a Mettler FP82 hot-stage and a Mettler FP90 central processor, was used to observe the thermal transitions and to analyze the anisotropic texture. The spectra of ATR-FTIR were recorded on a Bruker Tensor 27 system with 2 cm^{-1} resolution.

The UV/Vis and the fluorescence spectra were obtained from a Shimadzu UV-1650PC spectrometer and a Hitachi F-4500 fluorescence spectrometer, respectively. DLS measurements were performed by using a

UNIPHASE He-Ne laser operating at 632.8 nm. The scattering was kept at 90° during the whole experiment. The maximum operating power of the laser was 30 mW. The detector optics employed optical fibers coupled to an ALV/SOSIPD/DUAL detection unit, which employed an EMI PM-28B power supply and ALV/PM-PD preamplifier /discriminator. The signal analyzer was an ALV5000/E/WIN multiple-tau digital correlator with 288 exponentially spaced channels. The hydrodynamic radius (RH) was determined from the DLS autocorrelation functions by the cumulants and the CONTIN methods by using the software provided by the manufacturer. The transmission electron microscope (TEM) was performed at 120 kV using a JEOL 1020 instrument. 3 μ L of an aqueous solution of sample was placed onto a holey carbon- coated copper grid, and 3 μ L of 2% (W/W) uranyl acetate solution was added for negative stain. The sample was deposited for 1 min, and excess solution was wicked off by filter paper and dried at 45 °C. The data were analyzed with Digital Micrograph software.

RESULTS AND DISCUSSION

Synthesis

In order to realize the effective self-assembly and water solubility, an appropriate length of coil chain was incorporated to finely tune the self-assembly properties. Poly(ethylene oxide) monomethyl ether with the number of repeating units of 17 has been commonly used in aquatic assembly, 1,1'-biphenyl was chosen as the rod component in an effort to manipulate π - π stacking interactions (Scheme 1). A phenolic hydroxyl group was incorporated at the end of rod segment of **1** and we conceived that the presence of both hydrogen bond and π - π stacking interactions could realize the self-assembly of rod-coil molecules. Molecules **1** were synthesized with relatively high yield by etherification of 4,4'-biphenol and a white waxy solid precursor **4**. The structure of **1** was characterized by ^1H -NMR and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy and was shown to be in full agreement with the structure presented in scheme 1 (Figs. S1 and S2).

Structures of Bulk State

Compound **1** is a wax-like light yellow solid and is thermodynamically stable proven by the heating and cooling DSC scans. Figure 1 shows the DSC heating and cooling traces of **1**, which exhibits a thermotropic liquid crystalline phase at 183.4 °C, and then converses to the isotropic liquid phase at 230.8 °C during heating. On slow cooling of **1**, from the isotropic liquid to liquid crystalline phase, the fan-like texture is observed by POM experiment which can preliminarily confirm the presence of an ordered smectic A phase (Fig. 2)^[24]. To confirm the self-assembling structure of **1** in the bulk state, X-ray scattering experiments were performed at various temperatures.

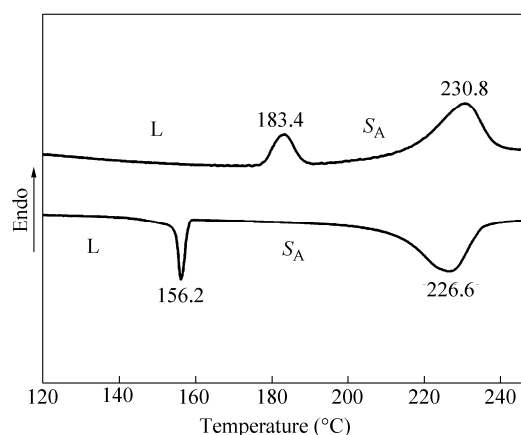


Fig. 1 DSC traces (10 K/min) of **1** recorded during the heating and the cooling scans

Figures 3(a) and 3(b) show X-ray diffraction patterns for **1** recorded at 180 °C and 80 °C on cooling from the isotropic phase to the solid state. In the liquid crystalline phases of **1**, several peaks in the small-angle region can be indexed as the (001), (002), (003) and (004) reflections for a 1-D lamellar phase with the layer spacing of 8.57 nm (Fig. 3a). Considering molecular length 9.62 nm (by Corey-Pauling-Koltun molecular modeling, Fig. S3) and POM experiment, we confirm that **1** self-assembles into a smectic A phase in the liquid crystalline state.

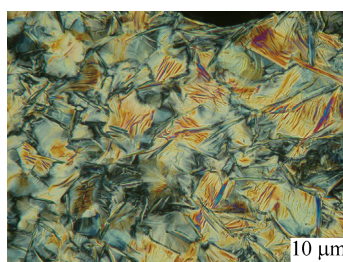


Fig. 2 Representative optical polarized micrograph of the texture exhibited by smectic A phase of **1** at the transition from the isotropic liquid during cooling

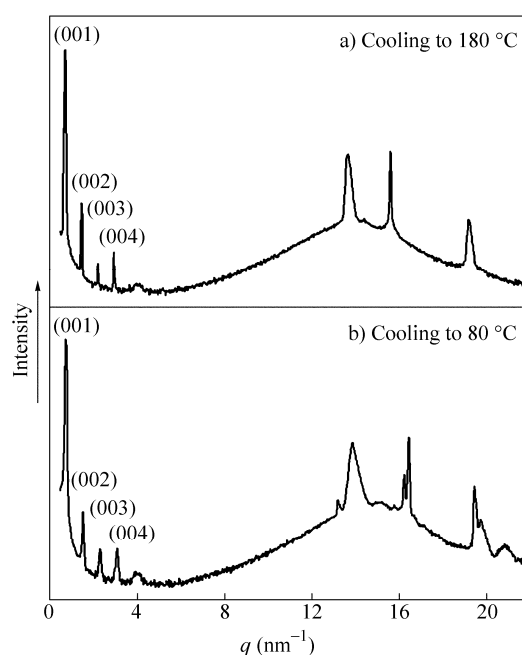


Fig. 3 X-ray diffraction patterns of **1**: (a) cooling to 180 °C and (b) cooling to 80 °C

Meanwhile, the wide-angle X-ray (WAXS) diffraction pattern shows three sharp peaks at q -spacings of 13.6, 15.5 and 19.2 nm⁻¹ that can be assigned as the (110), (200) and (210) planes, which appear due to crystal packing of the rod segments within the aromatic domain (Fig. 3a or Fig. S4)^[25]. The molecules pack in a rectangular lattice with unit cell dimensions of $a = 0.8$ nm and $b = 0.56$ nm. However, WAXS pattern of the conventional rod-coil molecules shows a broad halo peak in the liquid crystalline phase^[8, 19], and the ordered assembly of molecules **1** suggests that the rod segments may have hydrogen bond interactions besides π - π stacking interactions. In order to confirm our inferences, FTIR experiments were performed at room temperatures (Fig. 4). FTIR spectrum of **1** clearly shows that the peak assigned to the stretching vibration band of —OH at 3508.9 cm⁻¹ moves to low wave number and widens, which indicates that phenolic hydroxyl groups

at the end of rod block generate association, namely forming the hydrogen bond. In the ATR-FTIR spectra (Fig. 5S), when the temperature was heated to 140 °C, absorbance intensities from 3508–3302 cm^{-1} significantly decreased which may have been caused by the moisture in the sample. While the temperature reaches that of liquid crystalline phase, the relative intensities of peaks around 3302 cm^{-1} slightly decreased, yet have not disappeared which illustrated there were still weak hydrogen bond interactions between molecules in the liquid crystalline phase.

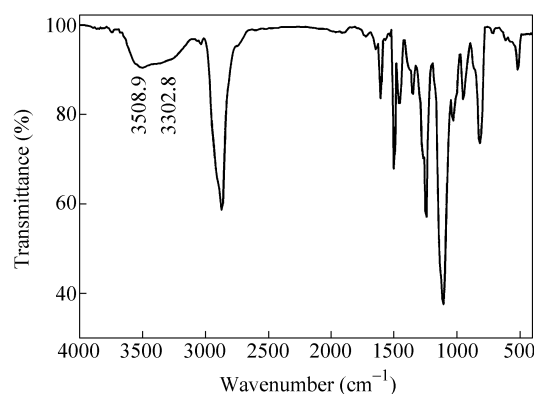
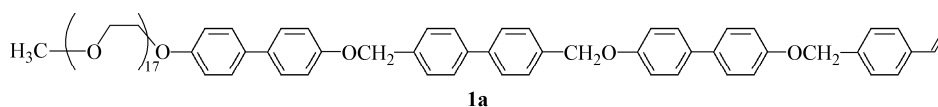


Fig. 4 FTIR spectrum of **1**

In the solid state phases of **1**, the SAXS patterns display several sharp reflections which correspond to equidistant q -spacings and are indexed to a lamellar lattice with the layer spacing of 8.34 nm (Fig. 3b). The WAXS pattern shows several sharp reflections that prove the ordered arrangement of the rod segments (Fig. 3b). On the basis of the data presented so far, the schematic representation of the S_A phase can be illustrated as shown in Fig. 8(a).

It's worth mentioning that rod-coil compound **1a** has the same coil chains but different rod segments as molecules **1** (Scheme 2) and has been reported by our previous work^[26]. The melting point of **1a** is 148 °C, and that of **1** is 230.8 °C, in general, prolonged rod will lead to the rise of melting point because the longer the rod is, the greater π - π stacking interactions are^[13]. However, in this paper, the melting point of **1** is higher than that of **1a**, which indicates the hydrogen bond plays a certain role in molecules **1**. In addition, molecules **1a** self-organize into the hexagonal perforated layer structure and molecules **1** self-assemble into S_A phase in the liquid crystalline state. The difference of self-assembling structure on heating can be explained by considering the coil segments to be conformational flexible and the interactions of rod blocks. On heating, higher thermal motion of flexible poly(ethylene oxide) coils relative to that of rods leads to expansion of coil chains, consequently requiring more interfacial area. The cooperative effects of π - π stacking, micro-phase separation and hydrogen bond interactions for molecules **1** make coil chains cannot destroy the stacking of rod blocks, but can only stretch and enlarge the interlayer spacing. Hence, molecules **1** self-assemble S_A phase and molecules **1a** form the hexagonal perforated layer structure with more interfacial area because of the lack of hydrogen bond interactions.



Scheme 2 The chemical structure of **1a**

Aggregation Behavior in Aqueous Solutions

Molecules **1** consisting of hydrophilic flexible chains and hydrophobic rigid aromatic segments, when dissolved in a selective solvent for one of the blocks, can self-assemble into an aggregate structure because of their

amphiphilic characteristics^[27–29]. The aggregation behavior of **1** was subsequently studied in aqueous solutions using fluorescence spectra. The fluorescence spectrum of **1** in chloroform solution (0.01 wt %) exhibits a weak emission maximum at 350 nm (Fig. 5), because the aromatic segments are unconjugated and molecules **1** are dispersed. However, the emission maximum in aqueous solutions is red-shifted with respect to that observed in chloroform solutions, and the fluorescence is significantly strengthened, indicative of aggregation of the unconjugated rod core segments. Dynamic light scattering (DLS) experiments were performed in aqueous solution (0.01 wt%) to further investigate the aggregation behavior. CONTIN analysis of the autocorrelation function shows a broad peak ranging from dozens of nanometers to hundreds of nanometers (Fig. 6a). The angular dependence of the apparent diffusion coefficient (D_{app}) was measured, because the slope is related to the shape of the diffusing species. As shown in Fig. 6(b), the slope was observed to be 0.004, consistent with the value predicted for elongated nonspherical micelles^[21].

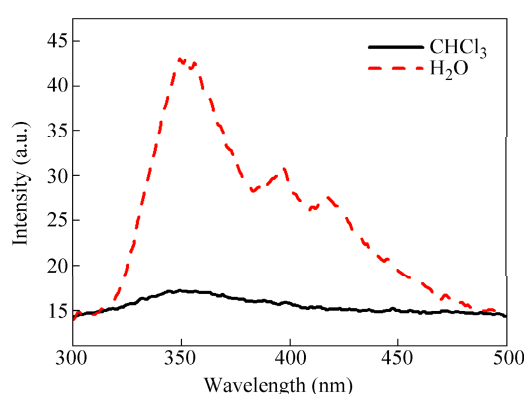


Fig. 5 Emission spectra of **1** in CHCl₃ (0.01 wt%) and aqueous solution (0.01 wt%)

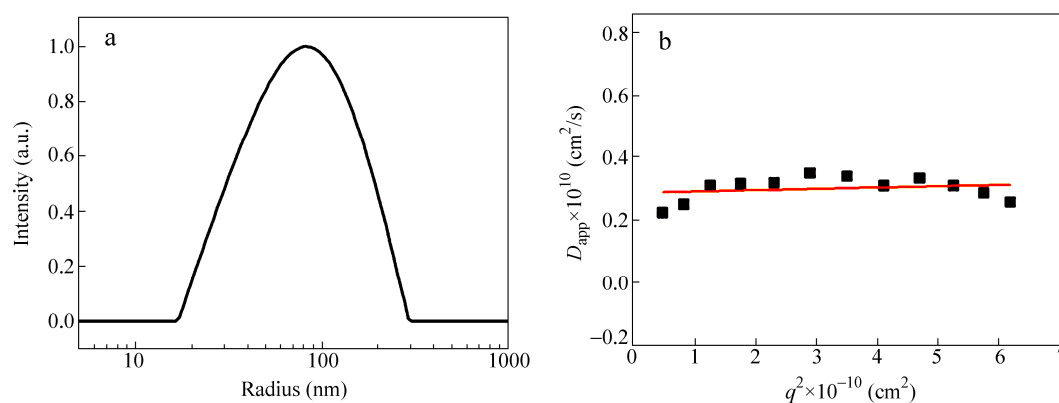


Fig. 6 (a) Hydrodynamic radius distribution of **1**; (b) Autocorrelation functions of **1** in aqueous solution (0.01 wt%)

The evidence for the formation of the cylindrical micelles was also provided by transmission electron microscopy (TEM) experiments. The TEM micrograph of **1** obtained from a 0.01 wt% aqueous solution clearly shows one-dimensional cylindrical micelles with a uniform diameter of $(13.0 \pm 0.5) \text{ nm}$ (Fig. 7). The length of the cylindrical micelles is dozens of nanometers to hundreds of nanometers, consistent with the hydrodynamic radius determined from DLS. Because the fully extended molecular length of **1** is estimated to be approximately 9.6 nm, the diameter width of 13.0 nm corresponds to one and a half molecular length, which imply there are two rod blocks in the direction of diameter. Hence, the cylindrical micelles comprised hydrophobic aromatic inner cores surrounded by hydrophilic flexible segments that are exposed to the aqueous environment, the schematic representation of the cylindrical micelles of **1** can be illustrated as shown in Fig. 8(b).

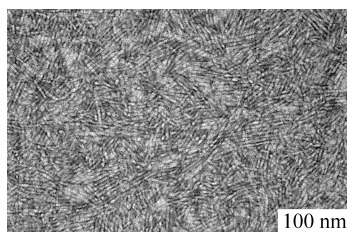


Fig. 7 TEM images (negatively stained with uranyl acetate) of sample cast from aqueous solution of **1** (0.01 wt%)

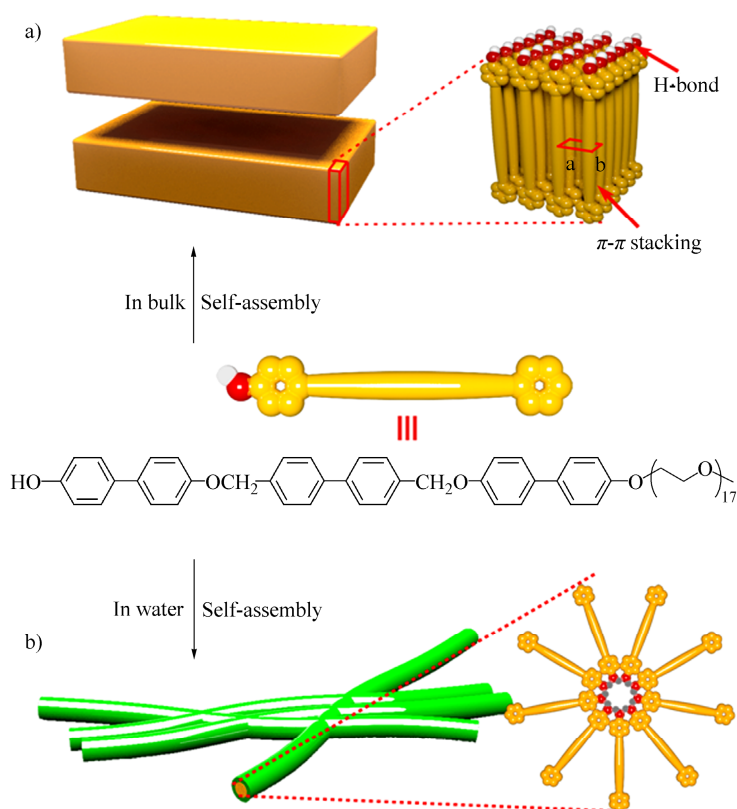


Fig. 8 Schematic representation of the proposed self-assembly of **1**: (a) S_A phase in bulk and (b) cylindrical micelles in aqueous solution

CONCLUSIONS

In summary, we reported the synthesis and the self-assembled behavior of the aromatic amphiphilic molecules **1** consisting of three biphenyl units, which were linked with ether bonds, as a rigid rod segment and poly(ethylene oxide) with the number of repeating units of 17 as coil segments. In bulk state, molecules **1** self-assemble into 1-D lamellar structure in the solid state or smectic A phase in the liquid crystalline phase *via* the cooperative effects of π - π stacking, micro-phase separation and hydrogen bond interactions. In dilute aqueous solutions, molecules **1** were observed to self-assemble into cylindrical micelles with uniform diameter and length of hundreds of nanometers. The strategy described here can be used to tune the self-assembled structures of rod-coil block molecules. We believe that more phase structure will be built through regulating reasonably the synergy of π - π stacking, micro-phase separation and hydrogen bond interactions.

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