Formation of Molecular Bundles from Self-Assembly of Symmetrical Poly(oxyalkylene)−Diamido Acids

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Sodium salts of poly(oxypropylene)−trimellitic amido acid (POP−amido acid), prepared from the reaction of POP−diamines and trimellitic anhydride, were found to self-assemble into orderly molecular bundles. The POP−amido acid has a symmetrical structure consisting of a hydrophobic POP middle block (2000 g/mol) and four symmetrical carboxyl end groups. By dissolving in water and evaporating on a polyether sulfone film, the POP−amido acid molecules self-assembled into a unique array with average dimensions of 7−13 nm in width, 2−5 nm in height, and 20−50 nm in length, observed by atomic force microscope. Varied morphologies were also observed when varying the pH, solvents, evaporating rate, concentration, and substrate surface. Unlike the common surfactants of single head-to-tail structure and the naturally occurring phospholipids of one head and two tails, the synthesized POP derivative is a symmetrical structure of four hydrophilic heads and one long hydrophobic block. Through the complementary noncovalent bonding forces, the molecules tend to align into molecular bundles or loops as the primary structure. The formation of different morphologies is controlled by the intermolecular forces including hydrogen bonding, aromatic $\pi-\pi$ stacking, ionic charge, and hydrophobic interaction, in a concerted manner.

Introduction

Self-assembling behaviors of amphiphilic copolymers have been well-studied because of their important role to serve as a template for directing the formation of nanoparticle arrays.[1] Actually, self-assembly through intermolecular noncovalent bonding force into a nanoarray is a broad term that includes organic molecules in solution and inorganic subjects on solid substrate.[2] The "bottom-up" process used to fabricate electronic devices in the nanoscale often requires the first step of organic patterning before introducing functional inorganic nanoparticles.[3] The formation of such an organic array is thermodynamically favored through molecular interactions. This versatile approach can form different morphologies in a nanometer scale.[4] The use of surfactant molecules as self-assembling units in aqueous solutions has been widely investigated.[5] It is well-known that a surfactant may aggregate into micelles depending on the concentration and its critical micelle concentration (CMC). Below this concentration, the molecules simply dissipate individually or form small aggregates such as dimers and trimers.[6] In the literature, the self-assembled morphologies are reportedly diverse in shape such as spherical micelles, vesicles, lamellae, ribbonlike, mushroomlike, cylinders, bilayers, hemispheres, and hemicylinders.[7] Both low-molecular-weight surfactants and amphiphilic copolymers are able to aggregate into nanoscale patterns.[8]

Self-assembling behaviors at the solid−liquid interface may be more complicated than that in solution and involve possible noncovalent bonding forces[9] such as ionic bridges, hydrogen bonding, $\pi-\pi$ stacking, dipole−dipole interactions, and hydrophobic effects. Amphiphilic copolymers provide a wide range of structural variations compared to conventional surfactants and consequently a diversification of self-assembling behaviors.

For example, the "Gemini" surfactants, which have two hydrophilic and two hydrophobic tails in a symmetric arrangement, offer new self-aggregating features.[10] One of the great challenges in self-assembly is to develop the primary units that are capable of organizing into ordered states through their inherent noncovalent bonding characters in a controllable manner. From the organic structural viewpoint, amphiphilic copolymers have a broad capability of interacting with themselves or across other species such as inorganic particles and surface substrates.

The amphiphilic copolymers consisting of poly(oxyalkylene) blocks are known for their broad structural variations and adaptable industrial applications.[11] Potentially, this type of amphiphilic structure with a hydrophobic core and a hydrophilic shell may be useful for drug delivery.[12] Previously, we prepared several different classes of amphiphilic copolymers from poly(oxyalkylene)−diamines (POA−diamines) and investigated their surface-active properties.[13] In continuing to understand the correlation between structure and property, we take an approach of synthesizing a symmetrical amphiphilic copolymer, which consists of a lengthy POP middle block as the hydrophobe and four carboxylic acids as the hydrophiles. Their interfacial behaviors can be further influenced by changing the terminal carboxylic acids into the corresponding Na⁺ salts due to the increase in hydrophilicity. Here we report their self-assembling behavior on polyether sulfone film, a required inert surface in minimizing the interaction with the amphiphiles. Atomic force microscopy (AFM) was used to probe the formation of intermolecular arrays, and a possible mechanism is proposed to account for the self-assembling process.

Experimental Section

Materials. Jeffamine POP-2000, α,ω-diamine of poly(propylene glycol) with a molecular weight (M_w) of 2000 g/mol (averaged 33 oxypropylene repeating units) and abbreviated as

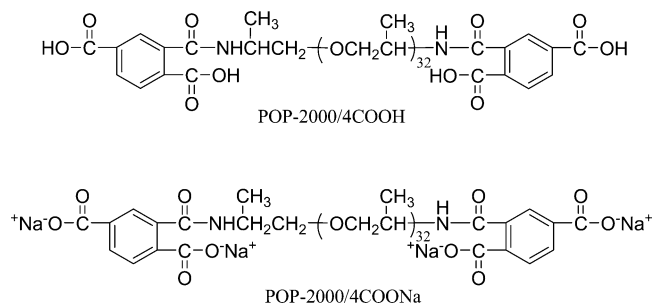* Corresponding author. Fax: +886-4-2287-1787. E-mail: JJLin@dragon.nchu.edu.tw.

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POP-2000/4COOH

POP-2000/4COONa

Figure 1. Chemical structures.

POP-2000, is a poly(oxypropylene)-backboned diamine with a amine content of 0.98 mequiv/g by HCl titration, obtained from Huntsman Chemical Co. or Aldrich Chemical Co. Trimellitic anhydride (TMA) was purchased from Aldrich Chemical Co. and purified by sublimation. Two amphiphiles, POP-2000/4COOH and POP-2000/4COONa, were synthesized from Jef-famine POP-2000 and TMA at a 1:2 molar ratio.

 Procedures for Synthesizing POP−Amido Acid Salt. The POP−amido acid amphiphile was prepared from the POP-2000 diamine and trimellitic anhydride at 1:2 molar ratio according to the following experimental procedures. To a 500 mL three-necked, round-bottomed flask which was equipped with a magnetic stirrer, nitrogen inlet−outlet lines, and a thermometer, POP-2000 (100 g, 0.05 mol) in tetrahydrofuran (THF; 150 mL) was charged and followed by a solution of TMA (19.2 g, 0.10 mol) in THF (50 mL) through an additional funnel. During the addition, the mixtures were stirred vigorously by using a mechanical stirrer and reaction temperature was maintained below 30 °C for 2 h. In the end of the reaction, the solvent was removed through evaporation under reduced pressure. The

TABLE 1: DFM Dimension by Means of Different Concentrations of POP-2000/4COONa

	DFM morphology[a]			
concn (wt %)	length[b] (nm)	width[c] (nm)	height[d] (nm)	diam[e] (nm)
0.1	10−15	5−8	2.3	10−40
0.4			3.1	30−90
0.6			3.3	30−100
0.8			3.6	30−100
1.0	20−50	7−13	3.5	50−100
1.2			3.1	30−100
2.0			6.1	30−100

 [a] Analysis by DFM: surface analyzer. [b] A piled length of molecular bundles in the vertical interaction. [c] Molecular bundle length which could match up the mathematic calculation of POP−amido acid. [d] Mean height of grain size with the standard deviation in 0.3 nm as the molecule on the substrate surface. [e] The POP−amido acid molecule diameter in DFM, which could be responding to the particle size of TEM measurement.

product in quantitative yield was obtained as a viscous light yellowish liquid and named as POP-2000/4COOH. By adding 4 equiv of sodium hydroxide, the amido acid was converted into carboxylic acid sodium salt (POP-2000/4COONa). The product was characterized by using FT-IR with the appearance of 1646 cm^{-1} for the amide absorbance and 1721 cm^{-1} for the carboxylic acid, and also by NMR. ^{1}H NMR (ppm): δ 0.97−1.12 (-CH$_3$ of oxypropylene), 3.45−3.56 (-CH- and -CH$_2$- of oxypropylene); 7.85 (d, J = 7.8 Hz, 1H), 8.36 (d, J = 7.8 Hz, 1H), 8.42 (s, 1H). ^{13}C NMR (ppm): δ 14.9−17.9 (-CH$_3$ of oxypropylene), 47.1−47.3 (-alkyl−N-), 69.3−75.5 (-OCH- and -OCH$_2$- of oxypropylene), 123−135 (aromatic ring), 166−167 (−C=O).

 Analytical Methods. Transmission electronic microscopy (TEM) was performed on a Zeiss EM 902 A and operated at
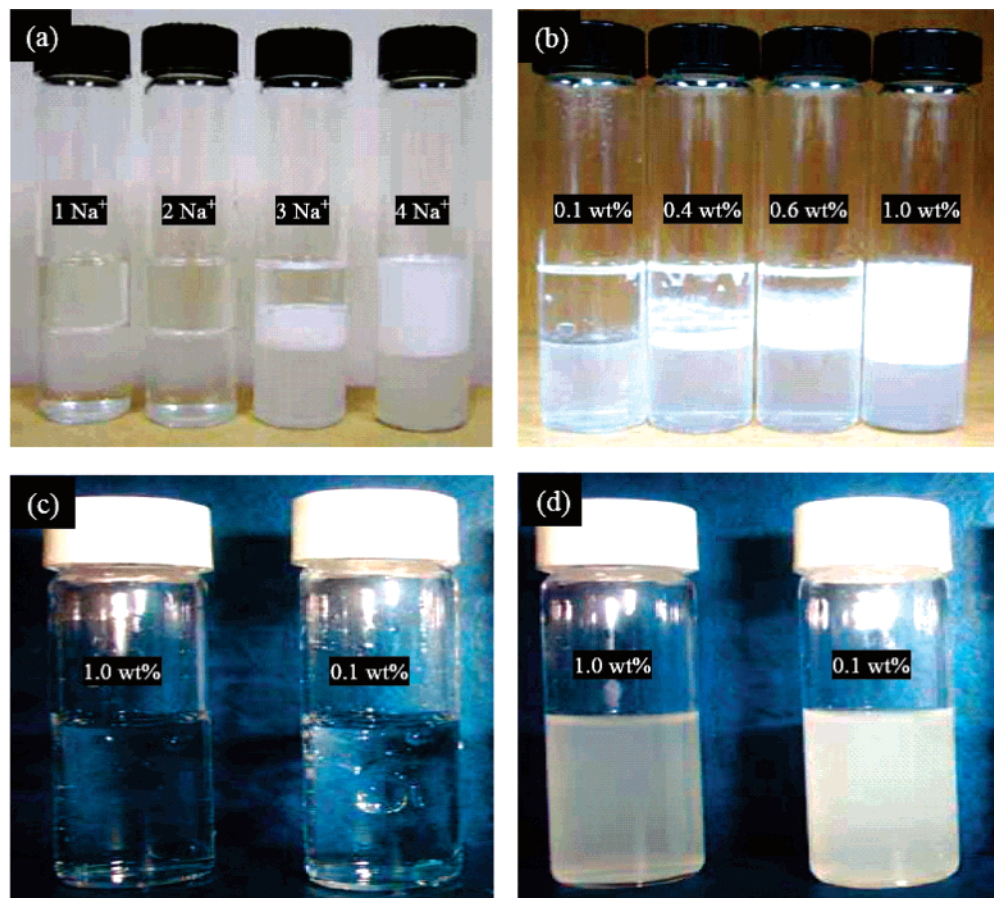

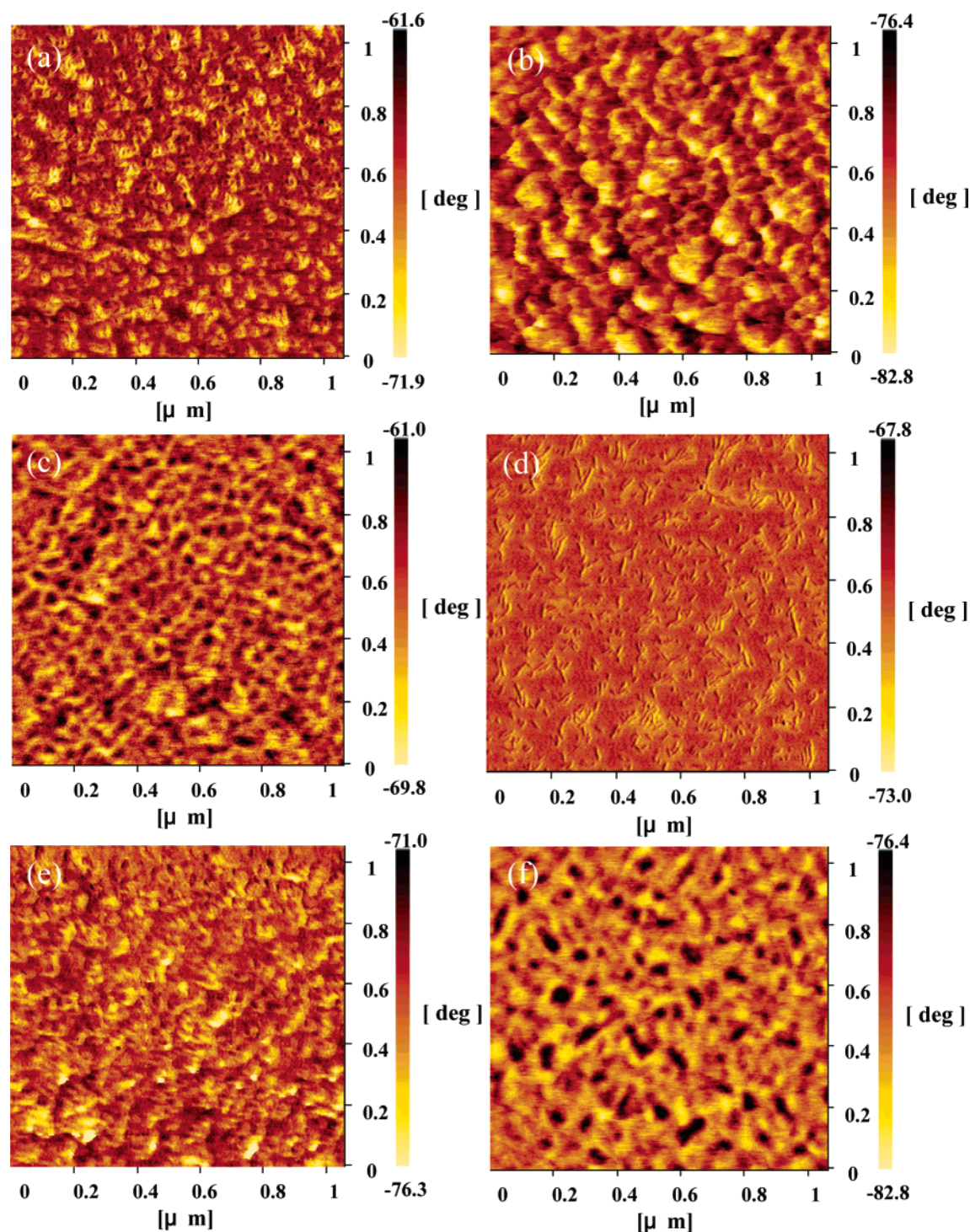**Figure 2.** Emulsion volumes and LCST of POP-2000/4COONa.

Figure 3. DFM images of POP-2000/4COONa.

80 kV, on a copper grid. The morphology of the poly-(oxypropylene) amido acid sodium salts on polymer film was analyzed by dynamic mode atomic force microscopy (DFM), all of which were carried out by using a SPA-400HV with an SPI3800N controller (Seiko Instruments Industry Co., Ltd.) at ambient temperature. The cantilever used was fabricated from Si with a spring constant of 16 N/m and a resonance frequency of 139 kHz. The DFM samples were prepared by dissolving POP2000/4COONa in deionized water and spin-coated onto a polyether sulfone (PES) film at a spin-coating rate of 500 rpm for 10 s and then 1500 rpm for 20 s. The interfacial tension was measured by the Wilhelmy method using a Kruss-K10 digital tensiometer equipped with a spherical ring. ^{1}H NMR and

^{13}C NMR spectra were recorded on a Varian Inova 600 MHz apparatus. Chemical shifts are given in δ; the coupling constants J are given in hertz. The spectra were recorded in solvents such as $CDCl_3$ at room temperature, and chemical shifts are given relative to the solvent signals. Fourier transform infrared spectroscopy (FT-IR) was recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer in the range of 400−4000 cm^{-1}; all samples were dissolved in THF and evaporated into thin film on a KBr plate.

Results and Discussion

Synthesis of the POP-2000/TMA Amphiphile. The amphiphile was prepared from the hydrophobic POP-2000 diamine

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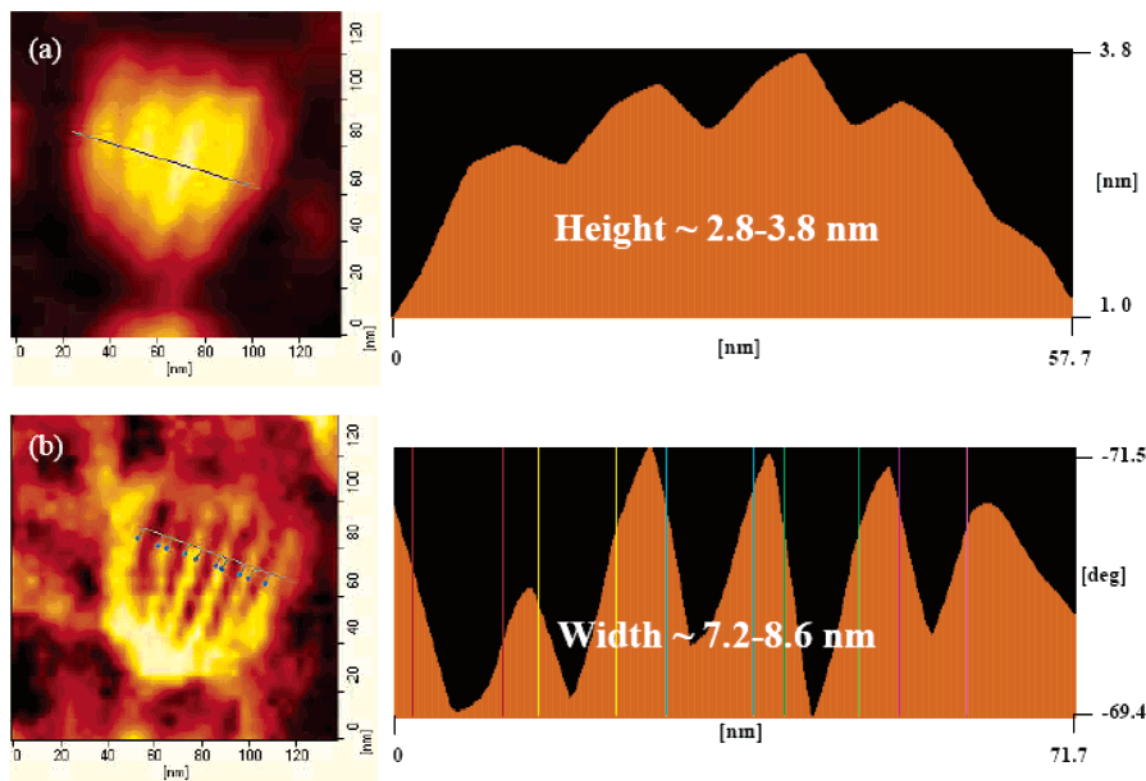*J. Phys. Chem. B, Vol. 109, No. 28, 2005* **13513**

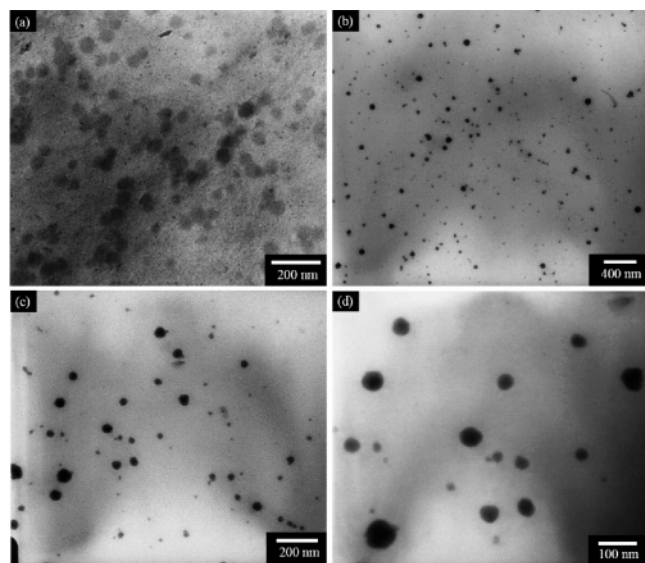**Figure 4.** DFM images of POP-2000/4COONa.

Figure 5. TEM image of POP-2000/4COONa.

and TMA at 1:2 molar ratio. The anhydride ring-opening reaction is straightforward at ambient temperature in a selective manner. The compound has characteristic chemical moieties including a hydrophobic POP-2000 middle block, four carboxylic acid, and symmetric aromatic amide functionalities.

The original POP-2000/4COOH is water-insoluble. But after transforming the carboxylic acid functionalities into sodium carboxylates, the POP-2000/4COONa become water-soluble at room temperature. Their chemical structures are illustrated in Figure 1.

The two distinct characteristics in the structure rendered the ability to lower the toluene/water interfacial tension as low as 2–4 mN/m at the concentration of 0.01 wt %. One of the unique properties of temperature-responsive polymers is the presence of a critical solution temperature in water. At a critical solution temperature, the solubility of materials is suddenly changed. The LCST[14] is defined as the critical temperature at which a polymer solution undergoes a phase transition from a soluble to an insoluble state above the critical temperature, due to the presence of hydrogen bonding in water. The polymer may be precipitated from water solution with increasing temperature at LCST.

The POP-2000/4COONa is a temperature-response polymer since it exhibits a sharp phase transition in water at 26 °C (LCST). Below this temperature, the amphiphile is capable of emulsifying the toluene/water mixture (Figure 2). Under conditions of equal toluene/water volume fraction as well as amphiphile concentrations of toluene between 0.1 and 1.0 wt %, the emulsion volumes were measured.

Solutions of the amphiphile in the concentration range of 0.1–0.8 wt % in water were allowed to spin-coating on a PES film and then examined by DFM. No regular array was found in this concentration range. However, when the concentration is increased to 1.0 wt %, an orderly structure was observed. At the optimized concentration, the molecules change from random coil to orderly bundle aggregate due to the noncovalent bonding self-assembly. Increased concentration from 0.1 to 0.8 wt % had resulted in a featureless aggregate array. It appears that the self-assembly on a PES substrate requires a critical mass aggregation, a phenomenon similar to a surfactant critical micelle concentration in water (Table 1).

When the concentration reached 1 wt % (Figure 3d), bundlelike protrusions are clearly seen on the PES surface. The density gradually decreased with increasing concentration. These observations are reproducible with batches of experiments and over a broad coverage on the substrate surface. These results indicate that the intermolecular interaction of POP-2000/4COONa organizes the molecular alignments into a 2-D array.[15] Due to the charge interaction of the carboxyl ions, the POP-2000/4COONa molecules tend to form the independent bundle stripes through both the attracting and repelling forces.
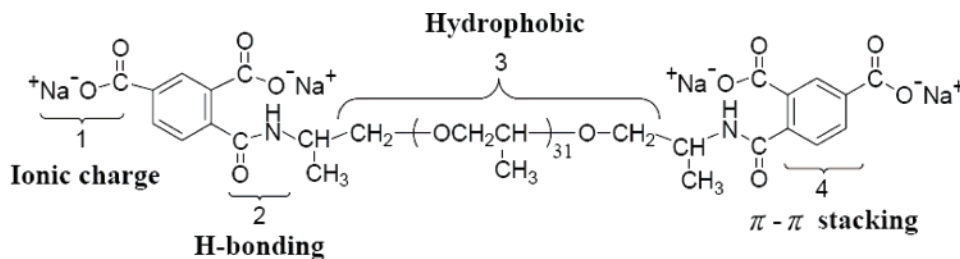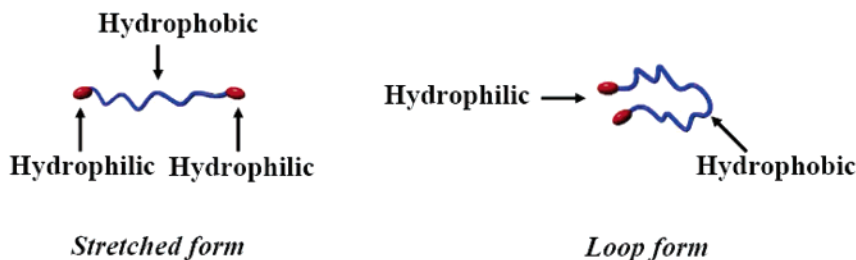
Figure 6. Conceptual diagram of self-assembly of POP-2000/4COONa.

Self-Assembly via a Stretched Molecular Shape To Form Molecular Bundles. The theoretical length of the fully stretched POP backbone was estimated on the basis of bond length (1.54 Å for C−C and 1.43 Å for C−O) and the bond angles (109.6 and 112°, respectively). It amounts to 109 Å for the POP-2000 backbone. The DFM images of POP-2000/4COONa are shown Figure 4a,b. A suitable substrate selection is an important requirement, because it may reveal the relationship between the amphiphile and the substrate surface. The polyether sulfone film is applied because of its smooth surface and minimum interference with the amphiphile self-assembly.

The mathematical calculation is based on the assumptions that the molecule is completely extended. However, the actual length as observed in DFM pictures is shorter because of intramolecular interaction.

Self-Assembly via a Curved POP Loop To Form Large Particles. The POP-2000/4COONa in water on the copper grid was found to assemble into spherical particles having a diameter of 50−100 nm cured, implying that the POP−amido acid sodium salts self-organized into spherical micelles in water (Figure 5). It is assumed that the spherical particles are the arrays derived from the primary POP loops.

Proposed Mechanism for the Self-Assembly. The conditions may alter the molecular stretch or the backbone curve during self-assembly. The symmetrical POP−amido acid is capable of associating intermolecularly in either a stretched form such as in the DFM image or a curved form shown in the TEM image, depending on the molecular environment (Figure 6). The unique morphology of the molecular bundles was formed via a mechanism involving the combined forces of noncovalent bond interactions, including hydrogen bonding, aromatic π−π stacking, Coulombic interactions, and the POP hydrophobicity.

Conclusions

A structurally symmetrical molecule consisting of a POP middle block and multiple sodium carboxyl functionalities was synthesized. The amphiphile was able to self-assemble into orderly molecular bundles or large particles depending on the concentration in water and evaporating conditions. The dimen-

sion of the molecular bundles was observed to be 7−13 nm in width, 2−5 nm in height, and 20−50 nm in length. The width is consistent with the calculated molecular length of 12.8 nm based on maximal bond extension. The unique formation of the molecular bundle is attributed to the designed structure containing multiple and complimentary noncovalent bonding interactions such as amide hydrogen bonding, aromatic π−π stacking, sodium ionic bridges, and the POP hydrophobicity.

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