Controlled Evaporation as an Easy Method of Constructing Novel Nano Objects from Amphiphilic Diblock Molecules

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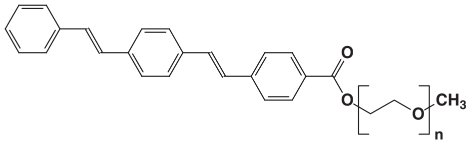
Novel nano ''island'' and ''ribbon'' morphologies could be fabricated just by changing the air-substrate interface of cast films during evaporation. Speeding up or slowing down evaporation of cast films 100-fold allowed diblock molecules containing oligo (phenylene vinylene) dimer as the rod segment and poly (ethylene oxide) as the coil segment to form two different self-assembled nano objects on mica: ''islands'' and ''ribbons,'' respectively.

Self-assembly has often been employed as a powerful approach to obtain nanoscale structures with well-defined shapes and functions.[1–3] A typical example is provided by rod-coil diblock oligomers, where the phase separation between the covalently connected segments leads to self-assembly into lamellar, cylindrical, spherical, and other structures, due to the incompatibility and volume fraction of both blocks.[4–7] When a photo-electronic segment is employed as the rod, the molecular packing in these thin films will also be essential for optical properties and charge transportation.

The nanostructures of diblock molecules on surfaces are additionally related to the substrate and the process of film casting and solvent evaporation compared to diblock molecules in bulk states. In previous work,[8,9] we found that an in-plane anisotropic monolayer, which emitted polarized light, could be fabricated by controlling the quantity of the molecules on mica. Now we have fabricated nano islands and ribbons with rod-coil diblock molecules containing oligo (phenylene vinylene) (OPV) dimer as the rod segment and poly (ethylene oxide) (PEO with average $M_w = 750$ and 550) as the coil segment, respectively, as shown in Scheme 1. The curvy ribbons with uniform curvature radii have not been reported before for assemblies of rod-coil diblock molecules. This work offers an easy approach to construct novel nano structures.

Synthesis and characterization of EO16OPV have been reported previously.[9] UV absorption of EO16OPV at 317 nm in water solution (1.04×10^{-5} mol/l) is blue-shifted by 49 nm compared to the absorption of the OPV monomer at 366 nm (confirmed as reference),[8] which strongly suggests that aggregates have formed. We cast 10 µL of the sample onto a 1 cm^2 freshly-cleaved mica to explore the formation of nano structures depending on evaporation conditions. Atomic force microscopy (AFM) observation of the cast film was carried out with commercial instruments (Digital Instrument, Nanoscope III, Dimension 3000^{TM} and Multimode^{TM}), operating in tapping mode in air. Height and phase images were obtained simultaneously using a resonance of approximately 360 kHz for the oscillating probe and a scanning rate of 1.00 Hz. We used a set-point ratio of up to 0.60 for the investigation.



Scheme 1. Chemical structure of EOnOPV: $n = 16$, EO16OPV; $n = 12$, EO12OPV.

When the solvent of such cast films was evaporated over several hours, AFM images of the cast film presented island-like morphologies all over the mica as shown in Figure 1a. The height of the island shapes is uniformly equal to 6.0 ± 0.2 nm. Since the height of AFM and an additional 6.2 nm d-spacing measured by X-ray diffraction are less than the fully and freely extended length of EO16OPV which is 7.6 nm (estimated from a Cerius^2 molecular graphics program based on a zigzag conformation of PEO),[10] the flexible block PEO should be curled and act as a cushion-like layer for the island.

When we kept the as-cast films in a saturated atmosphere of water at room temperature for 3 weeks until the solvent completely evaporated, however, we observed a very different nano morphology, shown in Figure 1b. These curvy ribbons displayed similar curvature radii (550 ± 50 nm), homogeneous heights (12.1 ± 0.3 nm) and similar widths (60 ± 10 nm). The lengths of the ribbons were on the order of micrometers. We also observed isolated ribbons as long as 20 µm (Figure 1c) and an interesting morphology with the ribbon coiled 3 times to form a closed tri-rim ''loop'' (Figure 1d).

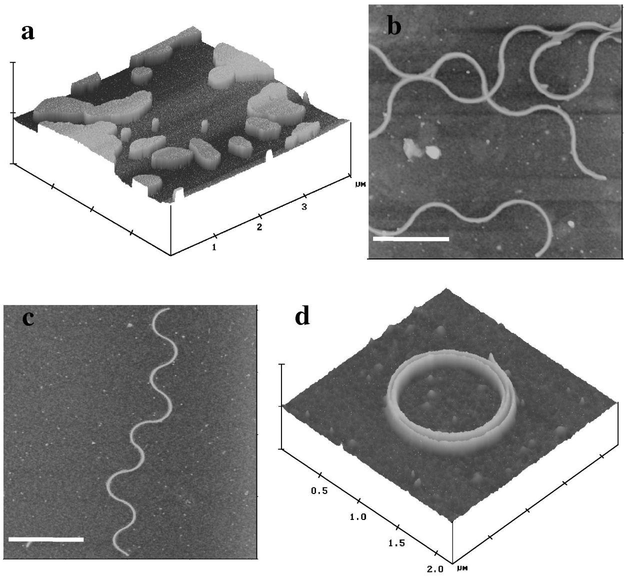


Figure 1. AFM height images (a) a 3-D representation of the nano islands; (b) (c) 2-D representations of the nano ribbons (the ruler for b is 1.5 µm and for c is 3.0 µm); (d) a 3-D representation of the coiled nano ribbon.

The corresponding phase images[11–13] of the islands are always lower than that for naked mica. In contrast, all phase images of the ribbons showed a higher phase degree than that of naked mica. In Figure 2a, for example, the height image shows both island and ribbon together; the corresponding section analysis for the island is 6.0 nm and for the ribbon 12.2 nm (Figure 2b). Their respective phase degrees showed that the island area was lower and the ribbon area was higher than the naked mica (Figures 2c and 2d).

The phase contrast is due to the mechanical properties of the molecules on the surfaces.[11–13] Different blocks on the outside should account for the observed phase contrast since EO16OPV is a diblock molecule. An AFM measurement of mica insufficiently covered by pure PEO ($M_w = 750$) revealed that the PEO domain had a higher phase degree than mica. In the monolayer islands PEO adsorbed onto mica, while the OPV block stretched outside (shown in Figure 2e) and showed a lower phase degree than mica. For the ribbon with a corresponding double height and a higher phase degree, a bilayer model with PEO outside shown in Figure 2f becomes reasonable.

We believe that the interface situation during evaporation is the major reason for such two different morphological forms. The high hydrophilic interaction between mica and the PEO segment under dry atmosphere causes the asymmetric arrangement of the islands shown in Figure 2e. Since PEO not only wets the hydrophilic substrate, but also the humid atmosphere by anchoring interactions with the air interface,[14] under humid air PEO outside can decrease surface energy, resulting in the bilayer ribbon as shown in Figure 2f, rather than the nano island structure formed under dry air as shown in Figure 2e. The mechanism for the formation of the homogeneous curvature radii of the nano ribbons is still not clear. We infer that the curvature radii might spring from the mechanical behaviour of the aggregates of EO16OPV during evaporation.[15]

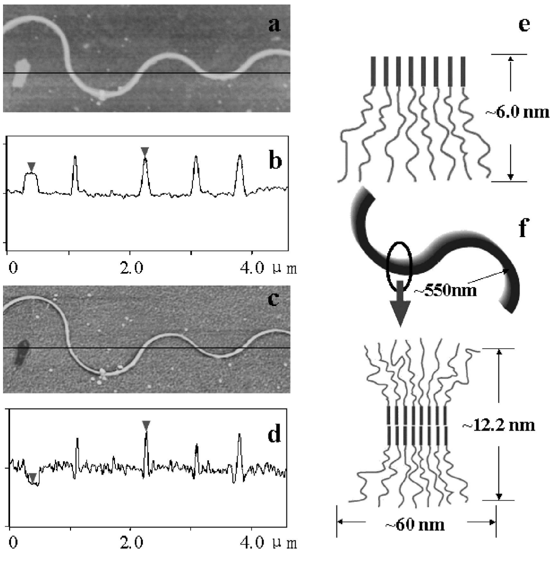


Figure 2. (a) The AFM height image of nano sheet and nano loop together; (b) Section analysis for the sheet and loop; (c) The phase image of nano sheet and nano loop together; (d) Section analysis of the AFM phase image; (e) The monolayer model for nano sheets; (f) The bilayer model for nano loops.

The ribbons formed on our EOnOPV are unique. No similar result has been reported for extensively studied systems such as Polyoxyethlylene glycol alkyl ethers (CnEm).[16,17] Our method of preparing the nano structures shown here is also reproducible for a very similar molecule with a shorter PEO chain, EO12OPV. With its fully extended length of 6.2 nm, we were able to prepare both island and ribbon shapes of this compound under similar evaporation conditions to those used for EO16OPV, but around 5 °C rather than room temperature. The islands of EO12OPV have uniform heights of 5.0 ± 0.2 nm measured by AFM and a 4.95 nm d-spacing by X-ray diffraction. The ribbons of EO12OPV have heights of 10.1 ± 0.5 nm, widths of 100 ± 20 nm, and curvature radii of 445 ± 20 nm. The corresponding phase degree of islands is also lower than mica, while that of ribbons is higher, agreeing perfectly with those of EO16OPV. The data support the monolayer model for islands and the bilayer model for ribbons.

This work offers an unusually easy method for constructing two distinct new nano shapes. We prepared nano island and nano ribbon morphologies just by changing the air-substrate interface of cast film during evaporation. Based on the AFM data, we propose that the nano islands are composed of a monolayer of the diblock molecule with OPV outside, and the nano ribbons are composed of a bilayer of the molecule with PEO outside. These well-defined shapes of nano structures might have a potential application in microelectronics and light emitting devices.

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