

Effect of the Cross-sectional Area of Polar Heads on Intralayer Packing of Photochromic Monodendrons

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Introduction

Recent studies of the interfacial behavior of branched amphiphilic molecules have focused on the effect of the cross-sectional mismatch between bulky polar heads and multiple alkyl tails [1, 2]. The cross-sectional mismatch between the dendritic shell and polar head determines their nontrivial packing structure as well as their physical properties at liquid and solid interfaces [3, 4]. In previous studies on the effect of reversing the cross-sectional mismatch, multiple alkyl tails were introduced to the same bulky crown ether polar head group, resulting in a transition from an orthorhombic supercell for the lowest generation to regular hexagonal lateral packing for the highest generation [5, 6]. In this work, we show the effect of the mismatch between the dendritic shell and a photochromic spacer group on the intralayer ordering of the single alkyl-chain molecules at the air-water and air-solid interfaces.

Methods and Materials

Grazing incident x-ray diffraction (GIXD) and reflectivity measurements [7-9] were conducted on a liquid-surface x-ray spectrometer at beamline 6-ID at the APS, as described elsewhere. The wavelength during the experiments was selected at 0.76 Å. A Langmuir trough was placed in a helium environment

to reduce the background scattering from air and to prevent the oxidation reaction that can damage the monolayer.

The three molecules used in this experiment consisted of a polar head group, a photochromic azobenzene spacer group, and a single 12-carbon alkyl tail. The polar head groups varied from a simple carboxylic acid group for the AA-1 molecule, an epoxy group for AE-1, and a bulky crown ether group for AD12-1 (Fig. 1). The synthesis of all three molecules was described elsewhere [10, 11]. The monolayers were prepared from a dilute chloroform solution with a concentration of 1.0 mmol/L. The cross-sectional area of the polar heads increased from 0.25 nm² for the carboxylic acid head group, to 0.30 nm² for the epoxy head group, and to 0.45 nm² for the crown ether head group, as determined by molecular modeling using the Cerius [2] package on an SGI workstation. In contrast, the known cross-sectional area for a single alkyl tail was 0.20 nm² [12]. As was clearly seen from the pressure versus area isotherms, the polar head groups dictated the cross-sectional area of the molecules at the air-water interface (Fig. 2).

Results and Discussion

Observational GIXD patterns showed that the AA-1 and AE-1 molecules formed ordered crystal structures

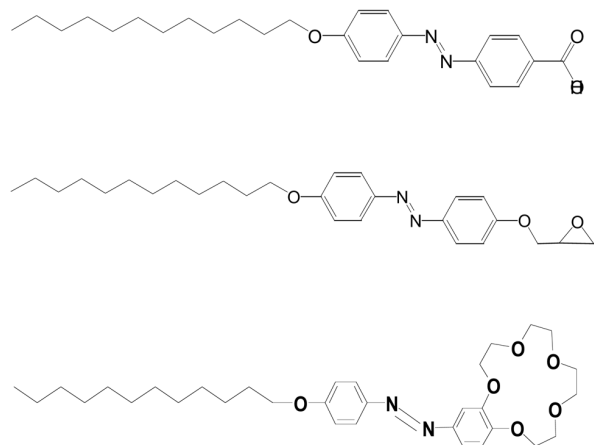


FIG. 1. Chemical formulas for AA-1 (top), AE-1 (middle), and AD12-1 (bottom).

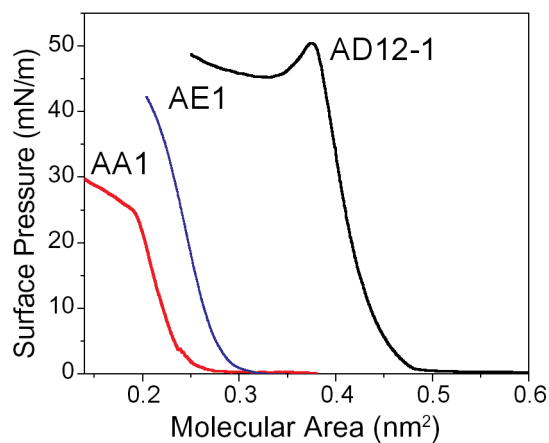


FIG. 2. π -A isotherms of AA-1, AE-1, and AD12-1.

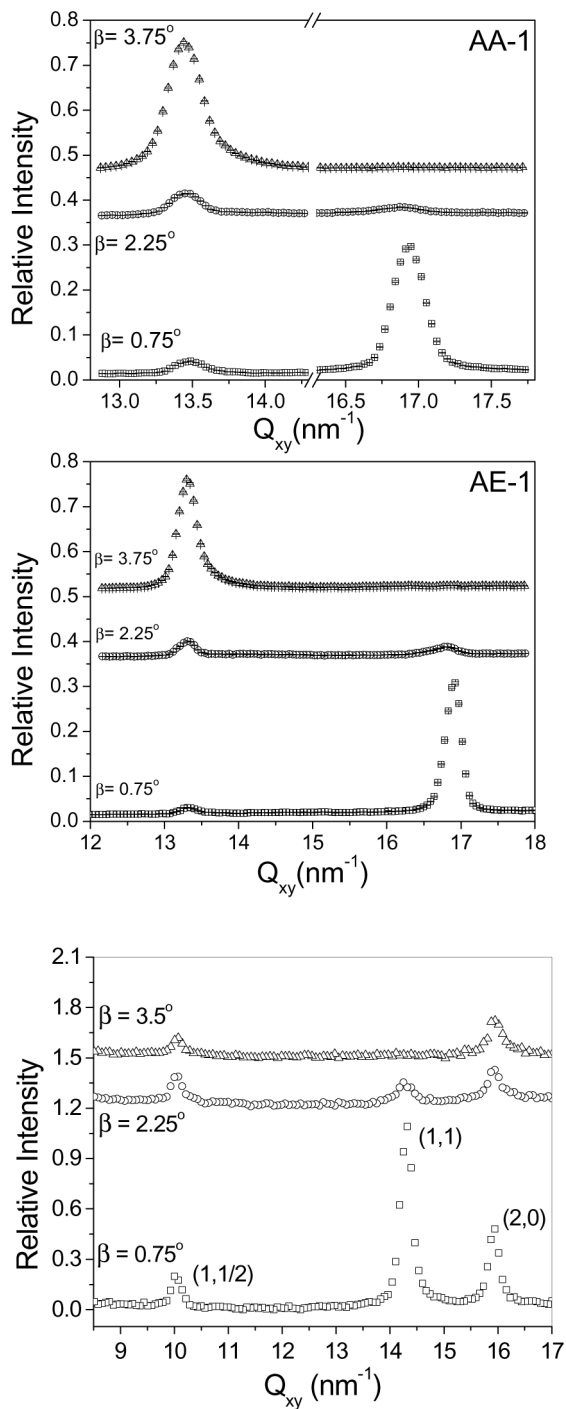


FIG. 3. High-resolution GIXD at the highest surface pressure. Panel a shows results for AA-1, panel b shows results for AE-1, and panel c shows results for AD12-1. The intensities are offset for clarity.

at all surface pressures, unlike the previously studied AD12-1, which formed ordered crystal structures only above 20 mN/m. Four peaks were observed for AA-1, with d-spacings at 0.467, 0.371, 0.316, and 0.230 nm, indexed as (1,1), (2,0), (2,1), and (3,1) peaks, respectively. Four peaks were observed for AE-1, with d-spacings at 0.472, 0.372, 0.319, and 0.231 nm, corresponding to (1,1), (2,0), (2,1), and (3,1) peaks, respectively. Unlike the AD12-1 molecule, neither AA-1 nor AE-1 appeared to have the lower Q peaks that are indicative of supercell structure.

High-resolution GIXD showed a highly favored tilted structure, with the (2,0) peak appearing at $\beta = 0.75^\circ$ and (1,1), (2,1), and (3,1) peaks appearing at $\beta = 3.75^\circ$ for both AA-1 and AE-1 molecules. The selective appearance of the diffraction peaks was best observed by high-resolution GIXD of the two lower Q peaks. As shown in Fig. 3a and 3b, the intensity of the (1,1) peak greatly increased as the β angle increased from 0.75° to 3.75° , while the intensity of the (2,0) peak greatly decreased. The selective appearance of all four peaks contrasted with the selective disappearance of the (2,0) peak seen for AD12-1 (Fig. 3c). At the highest pressures, the (2,0) peak for AD12-1 compound disappeared at higher β angles, indicating a selective tilt angle in the NNN direction.

The shift in the (1,1) and (2,0) peak positions indicated the decreased cross-sectional area per alkyl tail from 0.227 nm^2 for AE-1, to 0.223 nm^2 for AA-1, to, finally, 0.208 nm^2 for AD12-1. The correlation lengths for the molecules also decreased in a similar trend. The AD12-1 molecule with the bulky crown ether polar head had the highest-ordered crystal with the smallest unit cell of all three molecules. We believe the high degree of ordered structure was caused by the large cross-sectional area of the bulky crown ether polar head. The large polar head dominated the packing structure of the entire molecule, forcing a kinked packing structure. This structure negated any conformational influence of the azobenzene spacer group. However, the AA-1 and AE-1 had a polar head group with a smaller cross-sectional area than the azobenzene spacer group. The entire molecule formed a tilted packing structure to allow space for the azobenzene spacer and polar head group.

A comparison of rod scans and reflectivity for the three single molecules confirmed the tilted orientation of the tails as well as the dense packing of the molecules at the air-water interface. Detailed analyses of the molecules at the air-water and air-solid interfaces are currently being done. Additional studies of higher generations are the focus of another report [13].

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