Grazing-Incidence Diffraction Study of Amphiphilic Dendrimers

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Introduction

Molecular and supramolecular monodendrons and dendrimers provide powerful building blocks for the construction of giant macromolecular and supramolecular systems with complex architecture and precise shape and functionality. Dendritic building blocks self-assemble into cylindrical or spherical supramolecular dendrimers, which in turn self-organize into two-dimensional or three-dimensional lattices, respectively. The monodendron shape is determined by the molecular architecture of the repeat unit, the generation number, and the functionality both on the periphery and in the apex. Depending on the width of the aliphatic (peripheral) end and the apex (core), the monodendrons might be described as tapers, half-discs, discs, pyramids, cones, half-spheres, or spheres, with the result that in three dimensions they self-assemble into columnar or cubic macroscopic lattices. Less is known about the behavior of dendrimers at solid or liquid interfaces. Is the molecular shape near the interface the same as it is in three dimensions? How important are the chemical functionalities of the different parts of the molecule? When monolayers are formed, are they flat or composed of spherical, ellipsoidal, or cylindrical supramolecular structures?

We recently1 used pressure-area (Π-A) isotherms and x-ray reflectivity at the National Synchrotron Light Source (NSLS) to study a series of second- and third-generation monodendrons such as that shown in the inset to Fig. 1, with hydrophobic C12H25 alkyl tails at the periphery and hydrophilic COOHCO2CH3 or crown ether groups in the core. We found they were best described by a model in which the hydrophilic core is at or beneath the water surface, there is a low-density region just above the surface, and the alkyl chains form a high-density sublayer above the surface with the chains directed perpendicular to the interface. Specifically, we found that the molecular area was approximately proportional to the number of peripheral alkyl tails, and the layer thickness was approximately the fully extended length of one tail. These observations supported a "lamellar" model of the interface structure, but could also be consistent with hemispherical or hemicylindrical models. We have now performed the first grazing-incidence diffraction (GID) study of dendrimers at the air-water interface.

Materials and Methods

Samples were synthesized as previously reported1. We used the CMC liquid spectrometer at Advanced photon Source Beamline 9-ID-B. For reflectivity measurements, the outgoing beam was collimated by slits and measured with a NaI scintillation detector. For GID measurements the outgoing beam was collimated with Söller slits, with additional guard slits to prevent the primary reflected beam from entering the slits, and measured with a scintillation detector.

Results

Our reflectivity studies were limited to confirming that the electron density profile normal to the interface was consistent with that previously measured at the NSLS. A typical GID profile is shown below. In each of the two samples studied, we saw only one diffraction peak. These data are therefore insufficient even for lattice determination but can set a length scale for the surface structure. The peak shown in Fig. 1 corresponds to a distance d=2π/qa=40Å, approximately double the length of a fully extended chain. This allows us to rule out a purely lamellar structure for the Langmuir film in favor of a hemispherical or cylindrical model. We also found that sample damage was a serious consideration. After the sample had spent 20-30 minutes in the direct beam, the diffraction peak disappeared completely. It was necessary to time measurements carefully and translate the sample frequently to be sure that “missing” peaks had not simply been destroyed by the beam. Minimizing this effect will be an important consideration in designing future experiments.

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FIG. 1. A typical GID profile from the monodendron shown in the inset. Note the absence of higher order peaks, such as the two-dimensional (110) or (200). No other peaks were observed up to q=1.7 Å⁻¹.
References