

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 architectures and precise shapes and functionalities. Dendritic building blocks self-assemble into cylindrical or spherical supramolecular dendrimers, which, in turn, self-organize into 2-D or 3-D 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 are they composed of spherical, ellipsoidal, or cylindrical supramolecular structures?

Methods and Materials

We recently [1] used pressure-area isotherms and x-ray reflectivity at the National Synchrotron Light Source to study a series of second- and third-generation monodendrons with hydrophobic $C_{12}H_{25}$ alkyl tails at the periphery and with hydrophilic $COOHCO_2CH_3$ or crown ether groups in the core. Our observations were consistent with a “lamellar” model of the interface structure but could also be consistent with hemispherical or hemicylindrical models. We have now used grazing incidence x-ray diffraction at the APS to study structures of Langmuir films of first-generation monodendrons with two or three peripheral alkyl chains, as shown in Fig. 1.

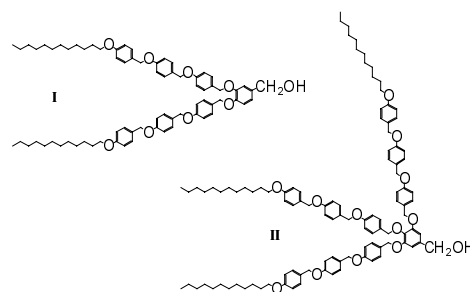


FIG. 1. Structures of two- and three-chain monodendrons studied.

We used the CMC-CAT liquid spectrometer at beamline ID-9-B. The outgoing beam was measured with a linear position-sensitive wire detector coupled with Söller slits, which permitted simultaneous measurement of the in-plane (Q_{xy}) intensity and the out-of-plane (Q_z) profile.

Results and Discussion

Pressure-area isotherms showed that the area per chain was on the order of 35 \AA^2 , only slightly larger than that expected for “bare” alkyl chains. Figure 2 shows diffracted intensity contours for compound I (two chains). The shift of the first peak to nonzero Q_z indicates that the molecules are tilted. A detailed analysis shows the molecules pack into a centered rectangular lattice (slightly distorted from hexagonal) with a 24° tilt of the chains toward the nearest neighbor.

Similar results were obtained for compound II, but, in this case, the chains tilted in a low-symmetry direction, with the result that the in-plane structure was an oblique lattice. Sample damage was a serious consideration in these measurements. Diffracted peak intensities would change dramatically or even vanish after tens of minutes in the direct beam. Minimizing this effect will be an important consideration in designing future experiments.

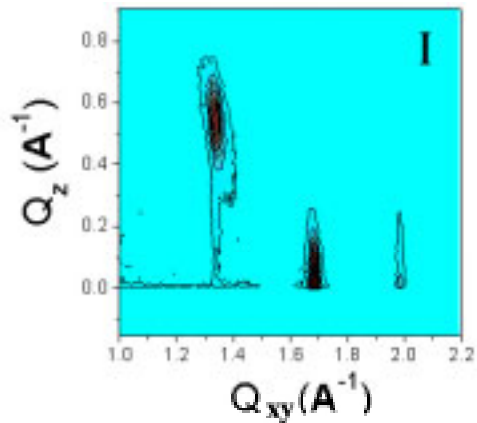


FIG. 2. Diffracted intensity from a Langmuir monolayer of monodendron **I**.

Acknowledgments

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Reference

[1] W.-J. Pao, M. R. Stetzer, P. A. Heiney, W.-D. Cho, and V. Percec, *J. Phys. Chem. B* **105**, 2170-2176 (2001).