Synchrotron Studies of Amphiphiles with Crown Polar Heads at Air-Water Interfaces

K. Larson,[1] D. Vaknin,[2] O. Villavicencio,[3] D. McGrath[3]
N. Stephenson,[1] V. V. Tsukruk[1]
[1]Department of Materials Science and Engineering, Iowa State University, Ames, IA, U.S.A.
[2]Ames National Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, IA, U.S.A.
[3]Department of Chemistry, University of Arizona, Tucson, AZ, U.S.A.

Introduction

The interfacial behavior of amphiphilic monodendrons with photochromic properties is an intriguing topic in the field of tunable organized molecular films. The mismatch of cross-sectional areas for polar heads and dendritic shells with multiple alkyl-terminated branches determines their nontrivial packing structure and the physical behavior of monolayers at solid and liquid surfaces (Fig. 1) [1, 2]. Recently, we proposed using bulky polar heads to balance dendritic shells and observed that the photochromic behavior of the Langmuir monolayers was, in fact, controlled by this cross-sectional mismatch [3, 4]. The initial formation of organized intralayer packing at the air-water interface is a key stage that governs their solid-state properties. In the present article, we report on synchrotron studies of amphiphilic photochromic molecules with bulky polar heads, such as those presented in Fig. 1. The molecules with more than one tail are currently under investigation.

Methods and Materials

X-ray grazing incident diffraction (XGID) and reflectivity measurements [5-7] were taken on a liquid-surface x-ray spectrometer at the 6-ID beamline at the APS synchrotron, as described elsewhere. The wavelength during the experiments was selected at 0.772 Å. A Langmuir trough was placed in a helium environment to reduce the background scattering from air and prevent an oxidation reaction that could damage the monolayer.

The **AD12-1** molecule presented in Fig. 1 consists of a large crown ether head attached to a photochromic azobenzene group. It has a single 12-carbon alkyl tail attached to the opposite end of the azobenzene. The synthesis involved was described previously [3]. The monolayers were prepared from a chloroform solution with a concentration of 1.0 mmol/L. A typical π-A isotherm is shown in Fig. 2. Molecular modeling with the Cerius[2] package shows a cross-sectional area of the polar head of 45 Å^2, while it is known that a single alkyl tail has a cross-sectional area of about 20 Å^2 [8]. As clearly seen in the isotherm, the large polar head controls the packing of the molecules.

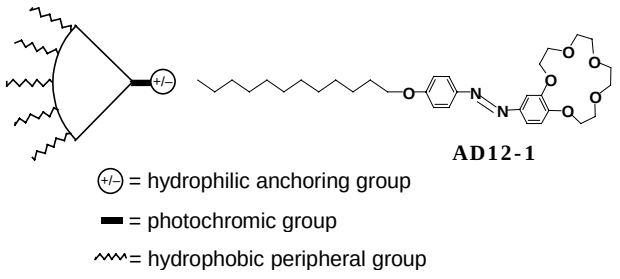

*FIG. 1. General scheme of amphiphilic monodendrons (left) and chemical structure of the **AD12-1** molecule with bulky crown-ether head, central photochromic group, and one alkyl tail (right).*

Results and Discussion

Figure 3 shows the XGID scan from the monolayer at 18 mN/m. XGID scans detected three peaks at surface pressures higher than 10 mN/m. The XGID pattern was fitted to Lorentzian-type curves with the peak positions corresponding to d-spacings of 6.26, 4.40, and 3.94 Å.

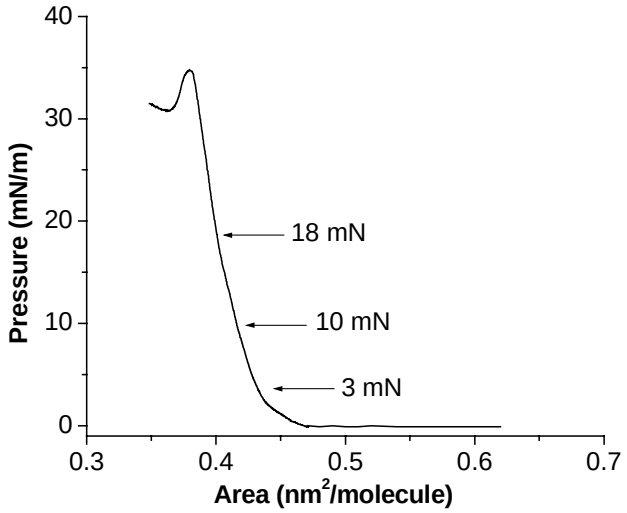

*FIG. 2. π-A isotherm for **AD12-1**. The surface pressures used in the x-ray experiments are labeled.*

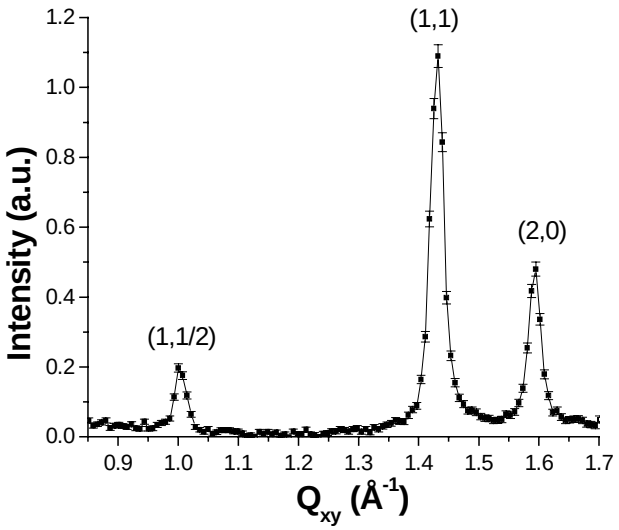

*FIG. 3. XGID scan of the **AD12-1** monolayer at higher surface pressure. Characteristic peaks for the (1,1/2), (1,1) and (2,0) planes are labeled.*

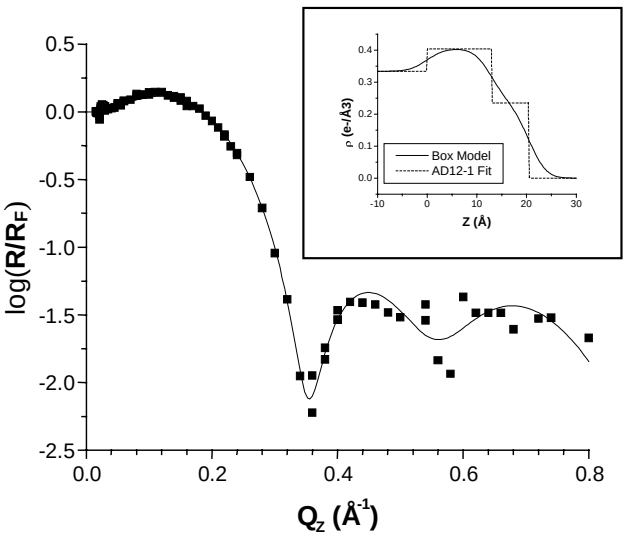

*FIG. 4. Reflectivity data for the **AD12-1** monolayer at a higher surface pressure. Squares indicate experimental data. The solid line is a simulation for model electron density. The insert shows the two-box model and corresponding smeared electron density distribution along the normal to surface plane.*

The two peaks with higher Q_{xy} values corresponded with values in the literature for (1,1) and (2,0) planes in an orthorhombic unit cell of polyethylene [9]. Calculations determined a unit cell size of 7.88 × 5.29 Å, which gave a cross-sectional area of 20.8 Å^2 per alkyl chain of the molecule. This value is within the known area for densely packed and tilted alkyl tails [8, 9].

Data from the rod scans supports the idea of molecules tilting in a preferred direction. We suggest that the additional peak at d = 6.26 Å corresponds to the supercell structure of the alkyl tails caused by the dense packing of polar heads.

The box model [10] was used to fit the data shown in Fig. 4 for the **AD12-1** monolayer at a higher surface pressure. The first box, corresponding to the azobenzene and polar head, has a length of 12.9 Å and an electron density of 0.41 e$^-$/Å^3. The second box, associated with the alkyl tails, has a length of 7.5 Å and an electron density of 0.24 e$^-$/Å^3. The distinction between the polar head and photochromic azobenzene fragment cannot be resolved within the current resolution. The length of the topmost box indicates that the tails are tilted toward the surface. The angle is estimated at 60º from the surface normal. The density of the tails extracted from the model is lower than the expected electron density of densely packed alkyl tails, which suggests the domain microstructure of the monolayer [11].

In conclusion, x-ray scattering of photochromic amphiphilic molecules at the air-water interface demonstrated that under higher surface pressure, a dense packing of the alkyl tails was formed with highly tilted tails and ordering that can be approximated with a two-layer density model.

Acknowledgments

The authors would like to thank A. Sidorenko, M. Lemieux, M. Lee, and D. S. Robinson for technical assistance. Funding from National Science Foundation Grant No. DMR-0074241 and Petroleum Research Fund Grant No. PRF 33867-AC7 is gratefully acknowledged. The Midwest Universities Collaborative Access Team (MU-CAT) sector at the APS is supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), through Ames Laboratory under Contract No. W-7405-ENG-82. Use of the APS was supported by the DOE BES under Contract No. W-31-109-ENG-38.

References

[1] *Dendritic Molecules*, edited by G. R. Newkome, C. N. Moorefield, and F. Vogtle (VCH, Weinheim, Germany, 1996).

[2] J. M. Frechet, Science **263**, 1711 (1994).

[3] M. Hashemzadeh and D. V. McGrath, Am. Chem. Soc., Div. Polym. Chem., Prepr. **39**, 338 (1998).

[4] A. Sidorenko, C. Houphouet-Boigny, O. Villavicencio, M. Hashemzadeh, D. V. McGrath, and V. V. Tsukruk, Langmuir **16**, 10569 (2000).

[5] C. Bohm, F. Leveiller, D. Jacquemain, H. Mohwald, K. Kjaer, J. Als-Nielsen, I. Weissbuch, and L. Leiserowitz, Langmuir **10**, 830 (1994).

[6] I. Weissbuch, F. Leveiller, D. Jacquemain, K. Kjaer, J. Als-Nielsen, and L. Leiserowitz, J. Phys. Chem. **97**, 12858 (1993).

[7] D. Vaknin and M. S. Kelley, Biophys. J. **79**, 2616 (2000).
[8] A. Ulman, *An Introduction to Ultrathin Organic Films* (Academic Press, San Diego, CA, 1991).
[9] V. M. Kaganer, H. Möhwald, and P. Dutta, Rev. Mod. Phys. **71**, 779 (1999).
[10] B. W. Gregory, D. Vaknin, J. D. Gray, B. M. Ocko, P. Stroeve, T. M. Cotton, and W. S. Struve, J. Phys. Chem. B **101**, 2006 (1997).
[11] K. Larson, D. Vaknin, O. Villacicencio, D. McGrath, and V. V. Tsukruk, J. Phys. Chem. **106**, 7246 (2002).