Neutron Diffraction Studies of the Structure, Growth, and Melting of Intermediate-Length $n$-Alkane Films Adsorbed on Graphite

H. Taub*, K. W. Herwig*, B. Matthies*, and F. Y. Hansen**

* Department of Physics and Astronomy and Missouri University Research Reactor Facility, University of Missouri-Columbia, Columbia, Missouri 65211, USA

** Department of Chemistry, Technical University of Denmark, DK-207-DTU, DK-2800 Lyngby, Denmark

Abstract—Over the past several years, we have conducted a variety of elastic neutron diffraction experiments to study the structure of films of two intermediate-length deuterated $n$-alkanes $[n$-CD$_2$(CD$_2$)$_{n-2}$CD$_3$] where $n = 24$ ($n$-tetracosane) and $n = 32$ ($n$-dotriacontane). The issues of interest in our studies include: the structure of monolayers deposited from an $n$-heptane ($n = 7$) solution as well as from the vapor phase, the melting behavior of these monolayers, the multilayer film structure, and the film growth mode. At room temperature, neutron diffraction patterns reveal striking differences between the molecular orientations, lattice constant, and coherence length of vapor-deposited and solution-deposited monolayers. Vapor-deposited monolayers of both molecules show qualitatively similar behavior upon heating. There is little change in their structure until reaching a temperature of about 340 and 350 K for $n$-tetracosane and $n$-dotriacontane, respectively, where a large thermal expansion begins, accompanied by a rapid decrease in the monolayer coherence length. Molecular dynamics simulations indicate that a melting transition is occurring in which there is simultaneous loss of both intrachain and interchain order as a result of the introduction of gauche defects along the chains. At higher coverages, diffraction patterns of vapor-deposited films of both molecules are consistent with crystallization of bilayer but not thicker films. Bulk Bragg peaks appear in the case of $n$-tetracosane at coverages between two and three layers, demonstrating incomplete wetting of the solid film as is found for films of shorter $n$-alkanes.

In this paper, we briefly describe our continuing neutron diffraction studies of the structure, growth, and melting behavior of films of flexible rod-shaped molecules. Our interest has focused on films of deuterated normal alkanes $[n$-CD$_2$(CD$_2$)$_{n-2}$CD$_3$] adsorbed on the basal-plane surfaces of graphite. Because the carbon backbone of these molecules consists of a series of saturated C-C bonds, these molecules form flexible chains of variable length $n$ with both bending and torsional degrees of freedom. The $n$-alkane chains may form part of a larger polymer molecule such as the nonpolar “tail” of lipid molecules. By themselves, the chains serve as prototypes for understanding the structure and dynamics of more complex adsorbed polymers.

We have used a graphite substrate for our experiments because it provides an inert surface to which the molecules can physically adsorb. It is favored by having a relatively small lateral variation in the molecule-substrate binding energy, the so-called “corragation” in the molecular adsorption potential. Since neutron scattering is not a surface sensitive probe, graphite also has the advantage of being available in high-quality powders of large surface area (>20 m$^2$/g) possessing very uniform basal-plane surfaces.

Most of our previous experiments have been concerned with studies of the shorter $n$-alkanes ($n \leq 6$) adsorbed on the graphite (0001) surface: their structure [1–3], phase transitions [1, 4], and dynamics [5, 6]. Here we discuss the extension of these investigations to the structure and melting of $n$-alkane films of intermediate length: $n$-tetracosane ($n = 24$) and $n$-dotriacontane ($n = 32$).

In Fig. 1, we show the neutron diffraction patterns of deuterated $n$-dotriacontane ($n$-C$_{32}$D$_{66}$, hereafter referred to as C32) monolayers [7, 8] adsorbed on an exfoliated graphite substrate (Gragefoil) [9]. These patterns (as well as those in Figs. 3 and 4) were taken at the Missouri University Research Reactor using a neutron wavelength of 4.35 Å. Elastic scattering from the graphite substrate has been subtracted.

The two diffraction patterns in Fig. 1 are obtained on films grown by different methods of deposition. In Fig. 1a, the C32 monolayer has been deposited from the gas phase as was the case in our studies of the shorter alkanes [1–6], whereas in Fig. 1b, it has been deposited from a liquid solution with $n$-heptane ($n = 7$). Deposition from solution was used in the early adsorption isotherm experiments [10–12] as well as in more recent

1 This article was submitted by the authors in English.
structural studies of these monolayers by scanning tunneling microscopy (STM) [13–15].

It is clear that there are quantitative differences in the diffraction patterns of the two C32 monolayers. The dominant (11) peak is both sharper and shifted to higher wavevector transfer \( Q \) for the solution-deposited monolayer in Fig. 1b compared to the vapor-deposited monolayer in Fig. 1a. Profile analysis of these diffraction patterns [7, 16] leads to the monolayer unit cells shown in Fig. 2. For the vapor-deposited sample of coverage 1.00 layers, we find the rectangular-centered unit cell shown in Fig. 2b with lattice parameters \( a = 87 \pm 1.5 \) Å and \( b = 4.64 \) Å. The molecules are oriented with their carbon skeletal plane parallel to the graphite (0001) surface (see Fig. 2a) as inferred from the good fit to the solid curve in Fig. 1a. This molecular orientation is also found for the herringbone monolayer structures of the shorter even-carbon-numbered \( n \)-alkanes [1, 2]. The width of the (11) Bragg peak corresponds to a coherence length \( L = 38 \) Å (about eight molecules wide) along the \( b \)-direction (see Fig. 2b).

On the other hand, we find a different monolayer structure corresponding to the model in Fig. 2d for the C32 film of thickness 1.21 layers deposited out of the heptane solution. The unit cell is still rectangular-centered, but the \( b \) lattice constant is now reduced to 4.26 Å. An intensity analysis of the (11) peak (not shown in Fig. 1b) favors an alternating parallel–perpendicular orientation of the molecules along the \( b \)-direction compared to the all-parallel and all-perpendicular configurations in Figs. 2b and 2c, respectively [7, 16, 17]. Note that in all of these models the long axis of the molecule is parallel to the graphite surface. The narrower (11) peak corresponds to a longer coherence
length of 120 Å in the b-direction for the solution-deposited monolayer.

We have found similar results for vapor-deposited and solution-deposited monolayers of n-tetracosane (n-C24D50, hereafter referred to as C24). The principal difference is that the lattice constant a = 65.0 ± 1.5 Å in the rectangular-centered cell is smaller due to the shorter length of the molecule. However, the same structural transformation and increase in coherence length occur on going from the vapor-deposited to the solution-deposited monolayer.

At this point, we have only a tentative explanation for the dependence of the monolayer structure on the presence of the solvent phase. Molecular dynamics (MD) simulations [18] show that, as the spreading pressure within a complete monolayer of the vapor-deposited structure (Fig. 2b) is increased isotropically, the b lattice constant contracts and some of the molecules reorient about their long axis so that their carbon skeletal plane becomes perpendicular to the surface. Potential energy calculations [16] have shown that the all-parallel structure of Fig. 2b has the lowest energy, if the b lattice constant is allowed to relax. However, if b is reduced to the value 4.26 Å, the alternating parallel/perpendicular structure of Fig. 2d has a lower energy than either the all-parallel (Fig. 2b) or all-perpendicular (Fig. 2c) structures [17]. MD simulations which include solvent molecules are now being undertaken [16]. Presumably, their effect will be to increase the spreading pressure in crystalline C24 and C32 monolayers at the graphite interface.

It is less clear how the presence of the heptane solvent increases the monolayer coherence length. Possibly there is molecular exchange between the adsorbed C32 (or C24) monolayer and the solvent phase. The increased mobility of the longer alkanes could result in an annealing effect in which the molecules return to the graphite surface with fewer gauche defects. We hope to test these ideas in future MD simulations now underway [16].

The structure of the C24 and C32 films above monolayer coverage is more easily investigated by neutron diffraction than by STM [13–15]. In Fig. 3, we show diffraction patterns from vapor-deposited C24 films measured at room temperature as a function of coverage [19]. The pattern at a coverage θ = 0.97 layers is similar to that shown for the C32 monolayer in Fig. 1a. It corresponds to a rectangular-centered cell with lattice constant b = 4.54 Å and with an all-parallel orientation of the molecules as in Fig. 2b. As the coverage increases to θ = 1.06 layers, a two-component line-shape develops. The (11) peak shifts upward to Q = 1.47 Å⁻¹, corresponding to the same d-spacing of 4.26 Å as for the solution-deposited C32 monolayer in Fig. 1b. However, a shoulder remains on the low-Q side of this peak at the position of the (11) peak at the lowest coverage. We interpret this pattern as resulting from the coexistence of two almost equally populated mono-

Fig. 3. Coverage dependence of the neutron diffraction patterns of vapor-deposited n-C24D50 films at room temperature. Unity coverage (θ = 1) is defined to be a complete monolayer having the rectangular-centered structure depicted in Fig. 2b with lattice constants a = 65.0 ± 1.5 Å and b = 4.54 ± 0.02 Å.

Fig. 4. Temperature dependence of the neutron diffraction patterns from vapor-deposited monolayers of (a) n-C32D56 (sample S1) and (b) n-C24D50 (sample S3). The solid curves are fits to the diffraction patterns using the model in Fig. 2b in which all molecules are oriented parallel to the surface. The dashed curves are Gaussian components which were included in the solid curve to improve the fit to the diffraction patterns. The physical origin of this Gaussian component which appears near the melting point of both monolayers is uncertain.
layer phases, one having the all-parallel structure of Fig. 2b and the other the alternating parallel/perpendicular structure of Fig. 2d [19].

At a coverage of $\theta = 1.94$ layers, the (11) peak has sharpened and the shoulder on its leading edge has vanished. Also, the $(h0)$ series of peaks at low $Q$ have increased in intensity. Profile analysis of this pattern is consistent with a crystalline bilayer in which the molecules in the second layer have the same alternating parallel/perpendicular orientations as shown in the monolayer model of Fig 2d [16] but are shifted $1/8$ of a lattice constant in the $b$-direction. This bilayer model conflicts with the one inferred from STM experiments by Watel et al. [15] in which all the molecules in both layers are in the parallel orientation, and the second layer is rotated $60^\circ$ with respect to the first about the surface normal.

As the coverage increases to $\theta = 2.91$ layers, the $(h0)$ series of peaks continues to increase in intensity and a shoulder reappears on the low-$Q$ side of the bilayer (11) peak near $Q = 1.4 \text{ Å}^{-1}$. This shoulder grows into a peak at the highest coverage of $\theta = 3.69$ layers.

We interpret these changes as due to the nucleation of bulk C24 particles in coexistence with the bilayer film. That is, at room temperature, the solid film incompletely wets the graphite substrate at a coverage between two and three layers.

This growth mode is the same as that found for the shorter $n$-alkanes ($n \leq 7$) on both graphite [1, 2] and Ag(111) substrates [20, 21]. Neutron diffraction experiments with films adsorbed on polycrystalline graphite substrates [2] and synchrotron X-ray scattering using single-crystal substrates [20] demonstrate that bulk particles grow quasi-epitaxially on the bilayer film with a specific crystal plane parallel to the film. In the case of butane on Ag(111), it was also possible to show that the bulk particles had a particular azimuthal orientation (about the surface normal) with respect to the bilayer film [20, 21]. We have not been able to go to high enough coverages with the intermediate-length C24 and C32 films adsorbed on graphite to perform the profile analysis necessary to determine whether the coexisting bulk particles grow with a particular plane parallel to the bilayer film.

To investigate the melting behavior of both the C24 and C32 monolayers, we measured their diffraction patterns as a function of temperature as shown in Fig. 4 [18]. The patterns for a C32 monolayer in Fig. 4a show only a slight shift of the (11) peak to lower $Q$ up to a temperature of about 350 K, indicating a very small thermal expansion. However, above this temperature there is a much larger thermal expansion and the peak broadens greatly. The diffraction patterns of the C24 monolayer in Fig. 4b show a similar temperature dependence, except that the large thermal expansion and peak broadening begin at about 340 K. This behavior is seen more easily in Fig. 5, where the coherence length in the $b$-direction, $L_b$, and the $b$ lattice constant are plotted versus temperature. Note that $L_b$ is inversely proportional to the leading half-width-at-half-maximum of the (11) peak.

From the temperature dependence of the diffraction patterns alone, we were unable to conclude that a melting transition was occurring in the C24 and C32 monolayers. Our studies of melting in monolayers of the shorter $n$-alkanes had shown an increase of the melting point with molecular length [1, 4] such that an $n$-hexane ($n = 6$) monolayer reached a melting point close to that of the bulk phase. Therefore, it seemed plausible for monolayers of the longer C24 and C32 chains to have melting points well above their bulk values of 324 and 334 K, respectively [22]. We also believed that it would be very difficult to thermally excite the vacancies needed for melting in monolayers of these longer $n$-alkanes. If the molecules were confined to the graphite surface, steric hindrance to molecular motion would simply be too great to allow the translational and rotational disorder characteristic of a fluid phase to develop.
In fact, MD simulations [18, 23] have shown that it is easier to introduce gauche defects into the adsorbed C24 and C32 molecules than we had anticipated. The gauche defects enter through the ends of the molecules by torsional motion about the terminal C-C bonds. They then propagate inward along the alkane chains, resulting in molecules with a more globular shape. This behavior is similar to that which we have found for monolayers of the shorter n-hexane molecules just below the melting point [4, 6]. It suggests that the "footprint reduction" mechanism of melting which we proposed earlier for monolayers of flexible rod-shaped molecules [4] can be extended to n-alkanes of intermediate length. In this mechanism, vacancies are introduced in the monolayer by out-of-plane motion of the molecules which reduces their footprint on the surface. These vacancies facilitate the rotational and translational motion needed to effect melting.

As will be discussed in an accompanying paper [23], the simulations indicate that there is a single temperature at which the gauche defects permeate the C24 and C32 chains and at which translational disorder appears in the monolayer [18, 23]. We refer to this temperature-induced phase transition in the monolayer as simultaneous "intrachain" and "interchain" melting. The transition temperatures calculated from the simulation agree well with the values of 340 and 350 K for C24 and C32, respectively, at which we observe the onset of a large thermal expansion and decrease in coherence length of the monolayers.

In summary, we find that the adsorption of intermediate-length n-alkanes on the basal planes of graphite provides a prototypical system for studying selective adsorption from binary fluid mixtures. The structural differences we have found between solution- and vapor-deposited monolayers provide a basis for interpreting quasi-elastic neutron scattering experiments now in progress to address the dynamics of selective adsorption. In addition, our neutron diffraction results on solid vapor-deposited films are consistent with the same growth mode leading to incomplete wetting which we found for the shorter n-alkanes. Finally, our diffraction experiments are in excellent agreement with MD simulations which indicate novel melting phenomena in monolayers of these intermediate-length alkanes.

ACKNOWLEDGMENTS

This work was supported by the US National Science Foundation under Grant no. DMR-9314235 and the Missouri University Research Reactor. We also acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

REFERENCES

9. UCAR Carbon Co., P. O. Box 94637, Cleveland, OH 44101.
17. More precisely, the intensity analysis favors approximately equal numbers of parallel and perpendicular oriented molecules. Potential energy calculations, in which the b lattice constant is fixed at 4.26 Å, yield the lowest energy for monolayer clusters with an alternating parallel/perpendicular configuration.