STRUCTURE AND DYNAMICS WITHIN MONOLAYER ORGANIC FILMS USING NEUTRON SCATTERING

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Introduction

There has been considerable interest in the structural and dynamical properties of ultrathin organic films [1-9]. Previous studies have shown that steric properties of simple molecules play an important role in the structure and dynamics within monolayer films adsorbed onto surfaces [1]. Such properties are fundamentally important to nanomechanical systems which make use of various molecular geometries [2].

To illustrate the power of neutron scattering to investigate the structure and dynamics within these systems, monolayer films of the *p*-phenylene (*p*-nP) oligomer molecules adsorbed onto the surface of graphite will be shown. Free *p*-nP molecules consist of n collinear phenyl rings twisted about the long molecular axis with respect to one another. In the crystal at room temperature the molecules are nearly planar and the monoclinic unit cell contains two *p*-nP molecules. These films are technologically significant due to their luminescent and wave-guiding properties [3].

Experimental Details

Individual monolayer films of the *p*-nP oligomers were grown *in-situ* onto the surface of graphite under conditions of thermal equilibrium at base pressure of ~10^{-3} torr. Each sample consists of approximately 11.2 g of 1.0 cm diameter graphite disks, with ~0.1 g of *p*-nP molecules adsorbed onto the surface, stacked within a cylindrical aluminum sample cell. Additionally, prior to film growth the graphite substrates were cleaned in-situ at a base pressure of ~10^{-3} torr at 450 °C for 3 days to remove surface contaminants, and the surface area was calibrated by a nitrogen adsorption isotherm at 77 K.

Structural measurements were carried out at the Intense Pulsed Neutron Source (IPNS) using the High Intensity Powder Diffractometer (HIPD). HIPD is primarily used to study small or weakly scattering samples, such as organic monolayer films adsorbed onto graphite. The instrument has an initial flight path of 6 m and a secondary flight path of 1 m,

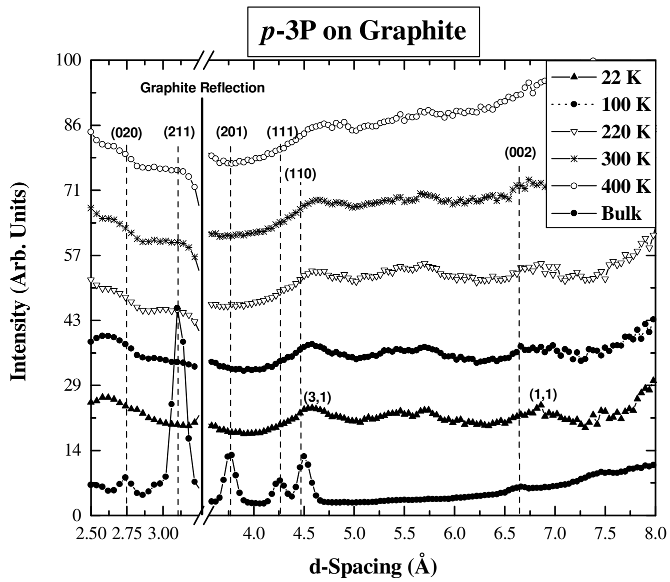

Figure 1: Diffraction data for a monolayer *p*-3P film at varying temperatures.

with detector banks at 90° and 30°, allowing the measurement of Bragg reflections with a d-spacing up to ~30 Å [4]. For this experiment, the 30° detector banks were utilized. Individual measurements were several hours each, carried out in the range 10K-370K.

The quasielastic neutron scattering experiments were carried out on the Disk Chopper Spectrometer (DCS) at the NIST Center for Neutron Research (NCNR) with an incident wavelength of 7.5 Å, resulting in an energy resolution of 0.035 meV full-width-at-half-maximum (FWHM). Neutrons were counted with 913 detectors spanning $-30° < 2\theta < 140°$. The neutron time of flight from the sample to the detector, t_{SD}, was measured across 1000 time channels in the range of 0.5-12.5 ms, with a constant channel width of 0.012 ms. This experimental configuration yielded neutron energy transfer within the range –334.75 to 0.92 meV (energy loss) when only the first frame of the neutron arrival times is considered. Data sets were typically collected in 4 hours at a range of temperatures from 22 – 370 K.

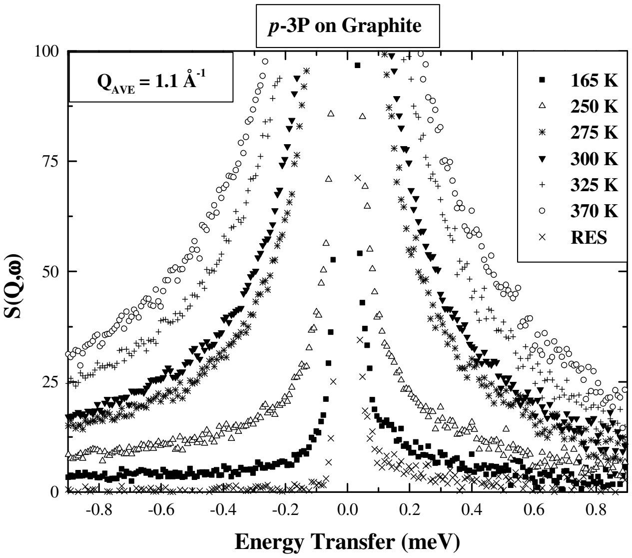

Fig. 2: Quasielastic spectra for the first monolayer of *p*-3P vapor deposited onto a graphite substrate.

Results and Discussion

HIPD results from an individual nominal one monolayer *p*-3P film adsorbed onto the surface of graphite are shown in Figure 1. After fitting the results to a Warren 2D profile the molecules are determined to be oriented with the long molecular axis parallel to the graphite surface. Similar results are obtained for *p*-4P and *p*-6P single monolayer films.

Quasielastic spectra from the DCS for a single-monolayer *p*-3P film are shown in Figure 2. An abrupt change in the character of the quasielastic signal indicates a phase change at approximately 300 K. Changes at both low and high Q-values have been identified and are consistent with translations along the surface as well as rotations about the long-axis, respectively. Similar results are observed for single monolayer *p*-4P films with an abrupt change in the nature of the scattering at ~315 K. For *p*-6P films, no change in the character of the scattering is observed within the measured temperature range.

Conclusions

It has been shown that monolayer films of the *p*-nP oligomers can be grown on graphite. Structure refinement of the diffraction data indicates that the long axis of the *p*-3P molecule lies parallel to the substrate. The *p*-nP films exhibit a change in the character of the molecule dynamics at about 300-315 K. As the length of the molecule increases, the temperature at which the character of the scattering changes also increases. The longest *p*-6P molecule exhibits no change in the character of the scattering within the limited experimental temperature range. Changes in the character of the scattering are observed at both small and large Q, indicating a change on both large and small length scales. These dynamics measurements indicate for each *p*-nP film a motion consistent with both reorientation of the rings about the long axis and translations along the surface are observed.

Neutron scattering is a powerful tool to study the structure and dynamics within ultrathin films at the film/substrate interface.

Acknowledgements

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