

Nanometer-Scale Structural, Tribological, and Optical Properties of Ultrathin Poly(diacetylene) Films

Robert W. Carpick*, Darryl Y. Sasaki, and Alan R. Burns

Sandia National Laboratories
Biomolecular Materials and Interfaces Dept.
PO Box 5800, Albuquerque, NM 87185-1413

* Current address: Engineering Physics Dept.
University of Wisconsin - Madison
1500 Engineering Dr.
Madison, WI 53706-1687

Introduction

The ability to create organized ultrathin films using organic molecules provides systems whose chemical, mechanical, and optical properties can be controlled for specific applications. In particular, polymerization of oriented mono- and multi-layer films containing the diacetylene group has produced a variety of robust, highly oriented, and environmentally responsive films with unique chromatic properties¹. These two-dimensional poly(diacetylene) (PDA) films, where the conjugation runs parallel to the film surface, have previously been prepared in a variety of forms²⁻⁵.

Of particular interest is the optical absorption of PDA due to its π -conjugated backbone. A wide variety of PDA materials, including bulk crystals, thin films, and solutions, exhibit a chromatic transition involving a significant shift in absorption from low to high energy bands of the visible spectrum, thus the PDA appears to transform from a blue to a red color. In addition, the red form is highly fluorescent, while the blue form is not. This transition can be brought about by heat⁶, binding of specific biological targets⁴ and applied stress(*mechanochromism*)⁷, among others.

In this paper, we discuss the Langmuir deposition of ultrathin PDA films and the subsequent measurement of their structural, optical, and mechanical properties at the nanometer scale. By altering the head group functionality, we can choose between mono- and tri-layer PDA film structures. Measurements with the atomic force microscope (AFM) reveal strongly anisotropic friction properties that are correlated with the orientation of the conjugated polymer backbone orientation. Furthermore, we can use the AFM tip or a near field scanning optical microscope (NSOM) tip to locally convert the PDA from the blue form to the red form via applied stress. This represents the first time that mechanochromism has been observed at the nanometer scale. Dramatic structural changes are associated with this mechanochromic transition.

Experimental

Materials. Details of our materials and sample preparation are described elsewhere⁸. Briefly, diacetylene molecules with two distinct head groups were made into separate films (Figure 1). The first, 10,12-pentacosadiynoic acid (PCDA) (I) (Farchan/GFS Chemicals) as a bluish powder which was purified to remove polymer content. The second molecule, N-(2-ethanol)-10,12-pentacosadiynamide (PCEA) (II) was prepared by coupling ethanolamine with 10,12-pentacosadiynoyl chloride in tetrahydrofuran and triethylamine. The acid chloride was prepared from the PCDA using oxalyl chloride in methylene chloride. PCEA was isolated by flash column chromatography on silica gel (25% ethylacetate/hexanes, $R_f = 0.23$).

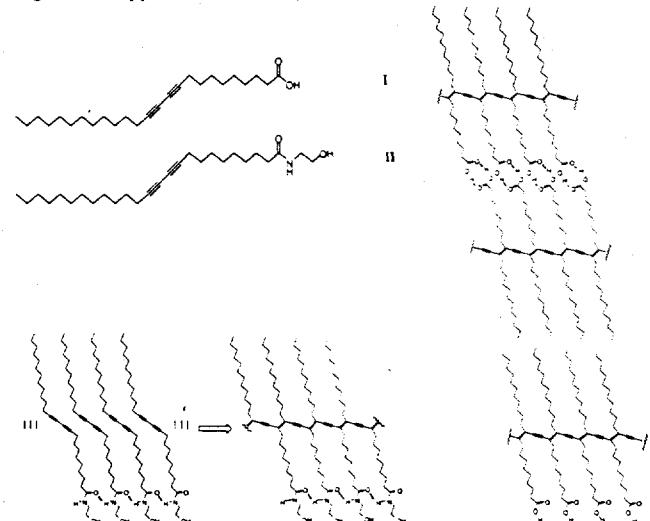
Film Preparation. Langmuir film preparations were performed on a Langmuir trough (Nima) which was situated on a vibration isolation table inside a class 100 clean room. The pure water subphase was kept at 15 ± 0.2 °C. Diacetylene monomers were spread on the water surface in a 50% chloroform/benzene solution. All films were incubated for 10 – 15 minutes at zero pressure prior to compression.

For UV polymerization at the air-water interface, the Langmuir films were first compressed to a surface pressure of 20 mN/m, then equilibrated for 20 – 30 minutes. UV irradiation of the compressed films was performed with a pair of pen lamps (Oriel). UV exposure was controlled by setting the lamp height above the air-water interface and choosing specific exposure times as described elsewhere⁸. A few minutes after UV exposure, the water was slowly drained off by aspiration. The films were laid down on mica (freshly cleaved) or silicon (piranha-cleaned) substrates that were presubmerged horizontally in the aqueous subphase before monolayer spreading. The substrate was then

removed and dried in cleanroom air. This horizontal transfer method proved to be the most effective for producing high quality films, as polymerization creates a certain amount of rigidity in the film on the water surface. This rigidity renders vertical transfer methods unreliable as the films would not uniformly compress during vertical transfer.

Instrumentation. A Nanoscope IIIA AFM (Digital Instruments) operating in contact mode was used to obtain topographic and friction force images. Measurements were acquired under laboratory ambient conditions at a scan rate of 3 Hz. Silicon nitride cantilevers (Digital Instruments) with a nominal normal force constant of 0.06 N/m were used for all measurements. A novel home-built NSOM⁹ was used to simultaneously observe sample fluorescence with sub-wavelength resolution as well as normal forces and shear forces. The tips used were Al-coated etched optical fibers. To record fluorescence, 488 nm light from an Ar laser is launched into the fiber optic. Filters are used to remove unwanted light such as 488 nm reflected light and Raman emission from the fiber. The sample fluorescence is focussed into a spectrometer (ISA/SPEX) and the signal is measured with a cooled photomultiplier tube and photon-counting electronics.

Figure 1. Upper left: PCDA (I) and PCEA (II) molecules. Lower left:



schematic of molecular orientation of II and its subsequent conversion to poly(II) upon UV irradiation. A hydrogen bonded network at the headgroup position is drawn. Right: poly(I) in its trilayer form.

Results and Discussion

Film Structure. Pressure-area isotherms indicate the amphiphiles of I and II on pure water both had identical take-off areas of $25 \text{ \AA}^2/\text{molecule}$, corresponding to the molecular cross-section of the hydrocarbon-diacetylene structure. The film of I collapses at low pressure ($\sim 12 \text{ mN/m}$), but upon over-compression reaches a stable solid phase with a limiting molecular area of $\sim 8 \text{ \AA}^2/\text{molecule}$. This over-compressed state corresponds to a stable trilayer structure. The film of II was stable as a monolayer with a collapse pressure of ca. 35 mN/m and an extrapolated molecular area at zero pressure of $25 \text{ \AA}^2/\text{molecule}$. After equilibration, films were polymerized to the blue-phase by exposure to incidence powers of $40 \mu\text{W}/\text{cm}^2$ for I and $23 \mu\text{W}/\text{cm}^2$ for II over a period of 30 sec. Red-phase films were produced by exposing the trilayer of I to $500 \mu\text{W}/\text{cm}^2$ and the monolayer of II to $40 \mu\text{W}/\text{cm}^2$ for 5 min.

AFM images of the blue- and red-phase forms of poly(I) and poly(II) on mica or silicon substrates confirm that the coverage for all films was nearly uniform for the entire substrate. Over 95% of the transferred film was flat to within $\pm 0.5 \text{ nm}$, with up to $100 \mu\text{m}$ crystalline domains observed. AFM film height measurements also confirmed that films of I and II formed trilayers and monolayers respectively. Furthermore, there were distinct height differences between the blue- and red-phase films of both I and II. The heights of the blue- and red-phase trilayer stacks of poly(I) were measured at 7.4 ± 0.8 and $9.0 \pm 0.9 \text{ nm}$, respectively. Similarly, the blue- and red-phase poly(II) monolayer films exhibited proportional height differences of 2.7 ± 0.3 and $3.1 \pm 0.3 \text{ nm}$, respectively.

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These results provide insight into the stabilization of diacetylene films. The headgroup interactions and alkyldiyne chain stacking should dominate the film structure of the monomeric diacetylene Langmuir films. The ability of the amide headgroup of II to form lateral intermolecular hydrogen bonded structures (Figure 1), similar to β -sheets in proteins, may explain the stability of this monolayer film on pure water. I films on pure water, in contrast, are unstable as monolayers but stack favorably into trilayers. Carboxylic acid dimer formation may aid in stabilizing this structure (Figure 1). Indeed, stable bilayer islands are commonly observed on top of the I trilayer. Thus, by altering the head group functionality, we can control whether the resulting film will be structured as a monolayer or a trilayer.

Friction anisotropy. AFM measurements indicate the films possess strong friction anisotropy¹⁰. For example, measurements on the red poly(II) monolayer (Figure 2(a) and 2(b)) reveal a domain structure. The friction force varies substantially from one domain to the next, and is nearly uniform within each domain. The topographic image reveals an essentially flat film. Topographic images within a single domain reveal parallel striations of varying width and uniform direction (Figure 2(c)), similar to previous reports⁶. The total height variation between these striations is ~ 2 Å. These striations are associated with the direction of the underlying polymer backbone, and allow us to determine the relative angle between the sliding direction and the backbone direction.

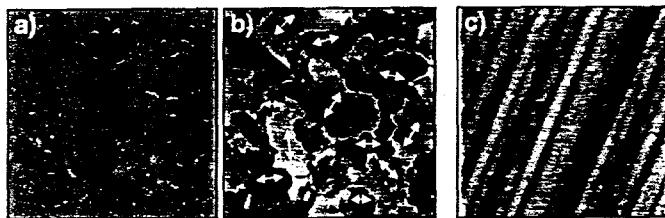


Figure 2. (a) $50 \times 50 \mu\text{m}^2$ AFM topography image of a red poly(I) monolayer. (b) simultaneous friction image. The friction image reveals the different domains. White arrows indicate the domain orientation. (c) A separate $500 \times 500 \text{ nm}^2$ AFM topography image of a single domain. The striations are indicative of the backbone orientation.

By measuring the friction force at zero externally applied load for different orientations, we find that friction is lowest when sliding parallel to the backbones, and 2.9 times larger when sliding perpendicular. This dramatic effect may be due to anisotropic film stiffness caused by anisotropic packing and/or ordering of the alkyl side chains, as well as the anisotropic stiffness of the polymer backbone itself. Along the backbone direction, the conjugated polymer bonds provide a rigid link between alkyl chains (Figure 1). However, the spacing between alkyl chains linked to neighboring backbones is determined by weaker interchain van der Waals' forces and possibly head group-substrate interactions. In other words, the lack of covalent bonding between neighboring polymer chains allows some freedom in their spacing, which has been observed previously for a similar PDA film⁶. Variations in film density would also explain the film height contrast observed in Figure 2(c)¹¹. The lower stiffness along the perpendicular direction may lead to larger molecular deformation when sliding in that direction, and thus a larger contact area and more gauche defect creation. These would both contribute to larger friction forces¹².

Mechanochromism. We have also observed that the blue-to-red transition can be activated at the nanometer scale using NSOM or AFM tips on both the trilayer poly(I) and monolayer poly(II)¹³. For example, Figure 3 shows simultaneous NSOM topography and fluorescence images on a blue poly(I) film. In the first scan (left pair), no fluorescence is seen over the flat PCDA region. In the subsequent scan (right pair), topographic changes are created, and localized fluorescence emission is produced. A fluorescence spectrum obtained over this region reveals the spectral fingerprint of red PCDA. These observations were reproducible. In general, when this transition is observed, the fluorescent regions grow gradually with each image acquired.

The blue-to-red transition has also been produced using AFM tips with both trilayer poly(I) and monolayer poly(II) blue films. With AFM, local topographic changes, discussed below, are observed *in-situ*. These changes indicate the transition is taking place. By creating a large ($>1 \mu\text{m}$) red region, *ex-situ* fluorescence microscopy is used to confirm that a red region has been

created by the AFM tip. With both AFM and NSOM, normal forces alone are not sufficient to cause the transition. Shear forces must also be applied, *i.e.* during the scanning process, to produce the blue-to-red transition. In all cases, the observed transitions are irreversible.

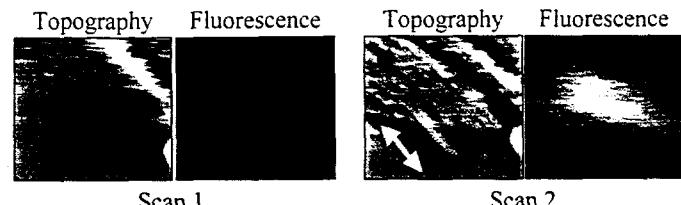


Figure 3. NSOM shear force topography and simultaneous fluorescence images ($2.4 \times 2.4 \mu\text{m}^2$) showing tip-induced mechanochromism.

The transformed regions consistently exhibit higher friction, increased roughness, and a surprising height reduction of typically 40-50%. High resolution images of the transformed regions, however, consistently reveal backbone-related striations. This indicates a substantial degree of preservation of the conjugated backbone despite the dramatic height reduction. No such structural change of PDA has been previously reported. While one might suspect that this height reduction could be explained by a removal of one or more layers in the trilayer poly(I) film, this cannot explain the comparable height reduction for the monolayer. While some molecules may well be removed during the transformation process, the film overall retains substantial integrity. One possibility is that the molecules adopt a highly tilted configuration. This is consistent with the observation that the transformation occurs more readily near cracks in the film. Such cracks would allow nearby molecules tilt substantially. The observation of larger friction forces in the transformed region is consistent with a highly tilted configuration, where one would expect a larger portion of the methylene groups to be in contact with the tip. The higher surface energy of these groups compared with methyl groups would likely produce higher friction. Molecular modeling efforts are being undertaken to investigate these structural changes in greater detail.

Conclusions

We have produced high-quality ultrathin PDA films using a horizontal Langmuir deposition technique. The number of stable layers in the film is controlled by altering the head group functionality. The films exhibit strong friction anisotropy that is correlated with the direction of the polymer backbone structure. Shear forces applied by AFM or NSOM tips locally induce the blue-to-red chromatic transition in the PDA films.

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