

# THERMOCHROMIC TRANSITIONS OF (POLY)DIACETYLENE MOLECULAR LAYERS

Robert W. Carpick<sup>1</sup>, Darryl Y. Sasaki<sup>2</sup>, Thomas M. Mayer<sup>2</sup> and Alan R. Burns<sup>2</sup>

<sup>1</sup> Engineering Physics Dept., University of Wisconsin-Madison  
1500 Engineering Dr., Madison, WI, 53706-1687

<sup>2</sup> Sandia National Laboratories  
PO Box 5800, Albuquerque, NM, 87185

## Introduction

Ultrathin organic films, prepared through methods such as Langmuir deposition or self-assembly<sup>1,2</sup>, offer the possibility of tailoring the optical, mechanical, and chemical properties of surfaces at the molecular scale. Such control of surface properties is required to implement micro- and nano-scale sensors, actuators, and computational devices. Materials that change in response to external stimuli are especially important for such applications. Poly(diacetylene)s (PDAs)<sup>3</sup> merit particular interest as these molecules exhibit strong optical absorption and fluorescence emission that change dramatically with various stimuli, namely UV absorption (*photochromism*)<sup>4-7</sup>, heat (*thermochromism*)<sup>8-10</sup>, applied stress (*mechanochromism*)<sup>7,11-13</sup>, changes in chemical environment<sup>14,15</sup>, and binding of specific chemical or biological targets to functionalized PDA side chains (*affinochromism/biochromism*)<sup>16-18</sup>. Chromatic transitions in PDA can even be studied at the nanometer scale, as we have recently observed through locally applied shear stresses with scanning probe microscope tips<sup>7,19</sup>. These transitions, along with other properties such as high third-order nonlinear susceptibility, unique photo-conduction characteristics, and strong nanometer-scale friction anisotropy<sup>20</sup>, render PDA an extremely interesting material.

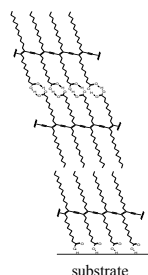
Optical absorption in PDAs occurs via a  $\pi$ -to- $\pi^*$  absorption within the linear  $\pi$ -conjugated polymer backbone<sup>3</sup>. These transitions involve a significant shift in absorption from low to high energy bands of the visible spectrum, so the PDA transforms from a blue to a red color. The mechanism driving these transitions is not understood in detail. It is believed that molecular conformational changes such as side chain packing, ordering, and orientation, impart stresses to the polymer backbone that alter its conformation, thus changing the electronic states and the corresponding optical absorption<sup>3,9</sup>. It is not established whether the transitions are continuous transitions or discrete transitions between two or more forms. The factors governing the degree of reversibility of the transitions are also not fully understood.

In this paper, we discuss chromic transitions in high quality tri-layer PDA films that are brought about by heat. A more detailed description of this work has been published elsewhere<sup>21</sup>.

## Experimental

**Film Preparation.** Details of our materials and sample preparation are described elsewhere<sup>22</sup>. 10,12-pentacosadiynoic acid (PCDA) molecules were obtained from Farchan/GFS Chemicals as a bluish powder which was purified to remove polymer content. 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  $15 \pm 0.2$  °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. The compressed film consists of three layers of PCDA (Fig. 1). UV irradiation of the compressed films was performed with a pair of pen lamps (Oriol) set at a specific height above the air-water interface. Following



**Fig. 1.** Sketch of the polymeric form of PCDA molecules. The polymerized form possesses extended linearly conjugated backbones that link the molecules together. The COOH head groups hydrogen bond to the silicon substrate and with each other. The polymer backbones, which lie parallel to the surface, are aligned in all three layers within a given domain of the film.

UV exposure the films were laid down on hydrophilic silicon substrates, pre-submerged horizontally in the aqueous subphase before monolayer spreading, by slowly draining water off by aspiration. The substrate was then removed and dried in cleanroom air.

**Temperature Studies.** A variable angle spectroscopic ellipsometer (J.A. Woollam Co., Lincoln, NE) was employed for ellipsometric studies of the thermochromic transition. Sample temperature during the measurements is controlled with a small home-built heat/cool stage consisting of a thermoelectric element attached to a copper block on which the sample is mounted. A solid-state temperature sensor and controller unit (Wavelength Electronics, Bozeman, MT) is used for temperature readout and regulation. Once equilibrated, the temperature was stable to within  $\pm 0.5^\circ$ . Ellipsometric measurements are made over the wavelength range 400 - 700 nm.

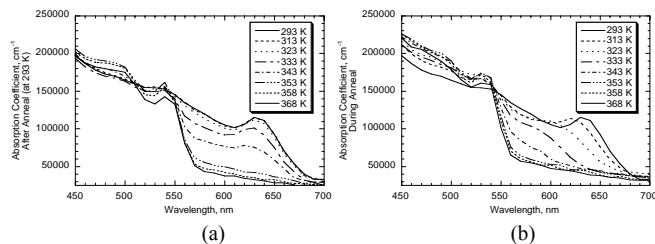
To obtain time-resolved measurements of the thermal transition, an optical platform incorporating a CCD spectrometer with fiber optic collection was set up to measure fluorescence spectra. The temperature was controlled with the same heat/cool stage used for the previous measurements. Poly-PCDA fluorescence was recorded using a fiber-optic coupled spectrometer (Ocean Optics Inc. Dunedin, FL), interfaced to a PC using LabView (National Instruments, Austin, TX) data acquisition control. Fluorescence spectra were acquired continuously with a 250 millisecond integration time per spectrum.

## Results and Discussion

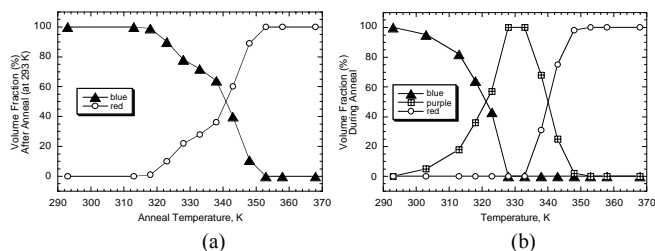
Thermochromic transitions of the poly-PCDA film were measured by ellipsometry and fluorescence on a film initially prepared in the blue form. The sample was annealed at a fixed temperature, and the measurement (ellipsometric or fluorescence) was acquired at that temperature. The sample was then quenched to 293 K, where a room temperature measurement was acquired. Subsequent heat-quench cycles were obtained at increments of 5 degrees. Shown in Fig. 2 are absorption spectra derived from the ellipsometry measurements. Fig. 2(a) shows the *room temperature* absorption after annealing to the indicated temperature. Fig. 2(b) shows the absorption obtained *at the annealing temperature*. The room temperature spectra demonstrate that the major absorption feature of the blue-form at 640 nm disappears and the red-form absorption features at 550 and 500 nm appear as the annealing temperature increases. At intermediate annealing temperatures, the 640 nm feature appears to shift to a shorter wavelength, resulting in an apparent new broad absorption feature at 600 nm. This feature is only observed at elevated temperatures and is not present in measurements made at room temperature either before or after annealing. Furthermore it is only observed upon annealing a film originally in the blue form. Material exhibiting this absorption feature we call the “purple” form of the material. Deckert *et al.*<sup>23,24</sup> have postulated the existence of an intermediate “purple” form based on kinetic aspects of the blue-to-red transition.

We can model the relative concentrations of blue and red form by assuming that the sample consists solely of blue form at the start of the annealing study, and solely of the thermochromic red form after annealing to 368 K. Then considering the film to be made up of a mixture of blue and red forms *at room temperature* after each annealing cycle, we construct an effective index of refraction for the film using the Bruggeman effective medium approximation (EMA). The resulting volume fractions are shown in Fig. 3(a). Starting at about 320 K, a significant fraction of the blue form is converted to red, with near complete conversion after annealing to 353 K.

Absorption spectra derived at each annealing temperature between 320 and 350 K indicate the shift of the blue absorption feature to the “purple form.” Assuming this to be a distinct form of the poly-PCDA, and that all blue form has been converted to purple at 328 K (where the purple feature is maximized), we apply a three-component EMA analysis to the spectra of Fig.



**Fig. 2.** (a) Absorption spectra determined from ellipsometric measurements obtained *at room temperature*, after annealing to the indicated temperatures. The sample is initially a blue poly-PCDA film. (b) The corresponding absorption spectra obtained *while annealing* at the indicated temperatures.



**Fig. 3.** (a) Volume fractions of blue and red form at room temperature after annealing to the indicated temperature. (b) “Effective” volume fractions of blue, purple and red form poly-PCDA in the film at the anneal temperature.

2(b). This gives the volume fractions of blue, purple and red forms at the annealing temperatures. The result is shown in Fig. 3(b). Examination of Fig. 3a and 3b shows that the purple form reverts primarily to blue after quenching to room temperature, with approximately 30% converting to red after annealing to 330–340 K and then quenching to room temperature.

The observed threshold temperatures of ~320 K to initiate creation of red poly-PCDA, and 353 K to establish nearly complete conversion to the red form, is similar to previous studies of other poly-PCDA films<sup>9,23,25</sup>. Collectively, these studies, along with ours, indicate that the optical properties of poly-PCDA films can be reversibly altered by heating up to approximately 320 K. Overall this change is far less profound than the changes that occur with full conversion to the red form, which occurs at ~353 K in our film.

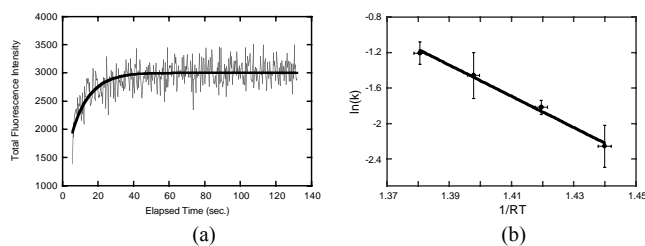
The purple form appears over the temperature range of 313 K to 343 K, and its appearance at these elevated temperatures is primarily associated with the disappearance of the blue form. Inspection of Figs 2(b) and 3(b) show that the purple absorption feature reaches its maximum intensity at about 330 K, while the blue absorption at 640 nm has largely disappeared. However, upon quenching to room temperature the blue form reappears and is still the predominant component of the film. We see no evidence for existence of the purple form at room temperature after any annealing step. The absorption maximum of the purple form shifts to shorter wavelength as the temperature increases with no apparent isosbestic point associated with the color transition. Since the purple form exists only at elevated temperature, it appears to be a metastable form that is interconvertible with the blue form.

These results lead us to propose that the purple form is a thermally distorted configuration of the blue form exhibiting a substantial shift of the absorption spectrum to shorter wavelengths. The purple form may represent a transition state in the conversion to the red form. However, our results indicate that it is energetically favorable for the purple form to revert to the blue, suggesting that the true transition state lies somewhat higher in energy and further along the reaction coordinate toward the red form. This conclusion is supported by the fact that no reversible behavior is seen in these films once they have been converted to the red form; annealing red films does not result in appearance of the purple form, nor conversion back to the blue form.

We have carried out first-order kinetic simulations to determine the reaction scheme by which the blue form converts to the red. Our data support a simple, first order, irreversible transition from blue/purple to red (B→R) for this film, where the purple form is simply thermally distorted blue material, involving a substantial shift in the absorption spectrum. A reaction scheme involving an independent purple phase produced via a significant structural transition involving energetic barriers between blue and purple forms is not consistent with our data.

Fluorescence studies establish that only the red form of poly-PCDA displays strong fluorescence. This is a general property of PDA materials, be they thin films, bulk samples or solutions. We can then obtain kinetic information for the irreversible transition to the red form by examining time-resolved measurements of fluorescence emission. Assuming first-order kinetics at fixed temperature, the amount of red [R] poly-PCDA is determined by:  $[R]/[R_{\max}] = 1 - e^{-kt}$  where  $[R_{\max}]$  is the final amount of red poly-PCDA.

Fig. 4(a) shows a typical plot of fluorescence intensity vs. time, in this case at 350 K, with a least-squares fit of the above equation. The rate constant at a fixed temperature  $T$  is given by  $k = A \cdot e^{-E/RT}$  where  $E$  is the energy barrier,  $R=1.9 \times 10^{-3}$  kcal mol<sup>-1</sup> K<sup>-1</sup> and  $A$  is the pre-exponential factor. Therefore, the slope of an Arrhenius plot  $[\ln(k) \text{ vs. } 1/RT]$  will be the energy barrier  $E$ . The result is plotted in Fig. 4(b). The linear behavior confirms that first-order kinetics provides an accurate description of this system. From the Arrhenius plot we determine  $E=17.6 \pm 1.1$  kcal mol<sup>-1</sup>. This result is somewhat lower than previous measurements<sup>23,24</sup> for multilayer films of PCDA Cd<sup>2+</sup> salts. The fact



**Fig. 4.** (a) Plot of fluorescence vs. time at 350 K (circles) with a least-squares fit of Eq. 1 (solid line). The fit provides a value of  $k$  for each measurement. (b) Arrhenius plot  $[\ln(k) \text{ vs. } 1/RT]$  of several measurements of fluorescence vs. time such as in (a).

that our films are only three layers thick, lack metal ion complexation, and are deposited on extremely flat substrates, may affect the kinetics of the transition significantly. In particular, our film is likely to exhibit fewer defects and stronger thermal coupling between and within layers due to their crystallinity and structural registry, thereby reducing the energy barrier.

## Conclusions

We have shown that spectroscopic ellipsometry can be used to monitor thermochromism in ultrathin poly(diacetylene) films. Spectroscopic ellipsometry reveals that trilayer films of poly-PCDA exhibit a partially reversible transition from the blue form to an intermediate purple form, followed by an irreversible transition to the red form. The purple form appears to be thermally distorted blue material. The purple form is present only at elevated temperatures and exhibits a large, reversible shift in the absorption spectrum to shorter wavelengths. Only the red form exhibits significant fluorescence emission. From time-resolved fluorescence experiments we determine an energy barrier of  $17.6 \pm 1.1$  kcal mol<sup>-1</sup> for the irreversible transition from blue/purple to red forms.

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