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Polarized fluorescence microscopy analysis of patterned, polymerized perfluorotetradecanoic acid–pentacosadiynoic acid thin films



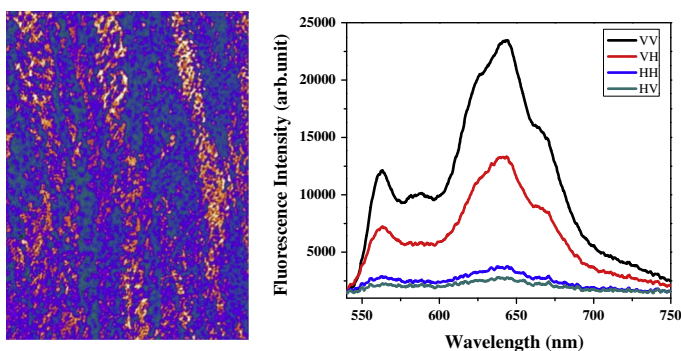
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HIGHLIGHTS

- Phase-separated mixed films underwent photopolymerization.
- Films formed oriented photopolymer fibers as determined by polarization microscopy.
- Fiber orientation induced by mechanical force during film deposition.

GRAPHICAL ABSTRACT



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ABSTRACT

Photoillumination of mixed films comprised of the photopolymerizable fatty acid 10,12 pentacosadiynoic acid and perfluorotetradecanoic acid deposited onto glass substrates gives rise to the formation of oriented polydiacetylene photopolymer fibers. The degree of polymer fiber orientation was investigated using dual-view, polarized fluorescence microscopy of the polydiacetylene, which allowed for characterization of individual fluorescent polymer fibers after photopolymerization, as well as comparison of the orientation of different fibers within the same sample. Measurements indicated that individual fibers consisted of multiple photopolymer strands with various orientations, and that there was a preferred orientation for fibers in the film as a whole. The fibers were preferentially oriented at an angle of approximately 60° to the direction of film compression during deposition from a Langmuir trough, with orientation being the result of mechanical stress exerted by the compression barriers coupled with rotation of the polymer fibers during film draining. These measurements were complemented with conventional “bulk” fluorescence polarization experiments, and compared with mixed film structures described previously for these systems at the air–water interface using Brewster angle microscopy.

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Introduction

Polydiacetylene (PDA) polymers are important technological materials for a variety of applications in biosensing, optical spectroscopy and non-linear optoelectronics [1,2]. These materials,

typically prepared by topochemical photopolymerization of $R-C\equiv C-C\equiv C-R'$ monomer units, undergo dramatic color changes upon application of heat (“thermochromism”), mechanical stress (“mechanochromism”) and analyte binding, often along with accompanying changes in their fluorescent emission properties. Most notable for the latter are transitions between a non-fluorescent blue polymer and a highly-fluorescent red polymer, believed to be caused by changes to the effective conjugation length of

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the polymer that accompanies mechanical or thermal perturbation. The luminescent properties of the polymer have been exploited in a wide-variety of applications, typically as a signal transduction mechanism for detection of analyte binding to thin polymer films (see [3,4] for reviews).

There is considerable value in preparing patterned films of PDA-based polymers for sensing applications, and there are a number of reports describing novel approaches for creating aligned PDA polymer films. Some of the more successful approaches include micro-contact printing, dropcasting, 3D replica molding and Langmuir Blodgett (LB) deposition [1,5–9]. Research in our group has focused on the latter; in particular, we are exploring the use of phase-separation of mixed surfactant films comprised of 10,12 pentacosadiynoic acid ($\text{CH}_3(\text{CH}_2)_{11}\text{—C}\equiv\text{C}(\text{CH}_2)_8\text{—COOH}$; PCDA) and perfluorotetradecanoic acid ($\text{CF}_3\text{—}(\text{CF}_2)_{12}\text{—COOH}$; PF), followed by LB deposition onto glass substrates for patterning [10,11]. In this approach, PF and PCDA are mixed at the air–water interface and the surfactants undergo phase-separation to give domains of either pure PF or pure PCDA. In addition to segregating the PCDA into well-defined regions of space, the PF also serves to stabilize the overall film through net attractive interactions between PF and PCDA. The film can then be photopolymerized with UV or laser illumination to yield the red fluorescent photopolymer product. A schematic illustration of the photopolymerization process and the resultant PDA polymer is shown in Fig. 1.

To date, we have explored several variations of this phase-separation approach for preparing patterned PDA photopolymer. For example, surfactant mixtures of 1:4 mol ratio (PF:PCDA) that were deposited onto glass substrates and subsequently photopolymerized with laser illumination (532 nm) yielded amorphous patches of polymer [11], while compression of the mixed surfactant films at the air–water interface, followed by photopolymerization with UV light at the air–water interface followed by deposition gave rise to the formation of phase-separated stripes of highly-fluorescent red PDA [10]. In this case, the compressive force applied to the films by the barriers of the Langmuir Blodgett trough during photopolymerization caused the resulting PDA regions to organize into stripes oriented parallel to the barriers (perpendicular to the direction of film compression). While this approach did give rise to a generally preferred orientation of the polymer material, the extent of photopolymer ordering was not particularly high and there was considerable organizational heterogeneity in the films.

In this work, we have explored an alternative preparation technique in which films with a significantly higher PF content (2PF:1PCDA) compared with those studied previously are deposited onto glass substrates and photopolymerized at the solid–air interface. We have found that this simple variation in preparation conditions favors the formation of linear aggregates (fibers) of PCDA, and that there is a generally preferred spatial orientation to the fibers. The degree of polymer orientation within a fiber and between individual fibers has been measured using polarized fluorescence microscopy, complemented by conventional fluores-

cence anisotropy and Brewster angle microscopy. The basis for the polarized fluorescence microscopy measurements is that a single conjugated PDA polymer chain can be reasonably modeled as a single emission transition dipole lying in the plane of the solid glass substrate [12,13], and thus, the fluorescence emission of the photopolymer is highly polarized along the length of the polymer chain. We have employed dual-view polarized fluorescence microscopy imaging in this work [14], in which the fluorescence emission from the sample is split into its constituent vertical and horizontal polarization components, which in turn allows determination of the spatial orientation of the emission transition dipoles in the photopolymer. Measurements have been complemented with conventional bulk polarization measurements on the film along with structural characterization using atomic force microscope and Brewster angle microscope imaging at the solid–air and air–water interfaces, respectively.

Materials and methods

Sample preparation

Perfluorotetradecanoic acid was purchased from Sigma–Aldrich Corp., and 10,12 pentacosadiynoic acid was purchased from Alfa Aesar. The solvents hexanes and tetrahydrofuran (HPLC grade) were purchased from EMD and Merck EM Science, respectively. All reagents were used as received. Stock solutions of mixed PF–PCDA were prepared by dissolving the solid surfactants in a 9:1 volume ratio of hexanes:THF, to yield a 2:1 mol ratio mixture solution of PF:PCDA. Microscope cover glass (VWR International) was rinsed with absolute ethanol and cleaned in a commercial plasma cleaner (Harrick Plasma) prior to use. Solutions and films were prepared and stored in the dark whenever possible in order to minimize exposure to ambient room light.

Films were prepared using a KSV 2000 Langmuir trough system (KSV-NIMA), at 22 ± 1 °C, with ultrapure water (Millipore, resistivity 18.2 M Ω cm) as a sub-phase. The sub-phase surface was cleaned thoroughly by suction before each experiment. The mixed surfactant solution was dotted onto the sub-phase surface and the solvent was allowed to evaporate for a minimum of 10 min before compression. Films were compressed at a rate 10 mm min⁻¹ to a surface pressure of 15 mN m⁻¹ (measured using a platinum Wilhelmy plate), were allowed to stabilize for ~20 min and were finally deposited onto a glass substrate using a single vertical upstroke. Films were allowed to dry in a clean environment before further measurements. Photopolymerization of the films was carried out directly on the fluorescence microscope described below, using the excitation laser as a light source.

Polarized fluorescence microscopy

Polarized fluorescence microscopy measurements were performed on a customized, wide-field epifluorescence microscope (Nikon TE2000, Nikon, Canada), using a 532 nm CW diode laser (100 mW, linear polarization, Dragon Laser Inc.) as an excitation source (Fig. 2). Polarization of the excitation beam was controlled by first passing it through a linear “clean-up” polarizer (Glan–Thomson) to ensure linearly polarized light, then converting it into circularly polarized light by directing it through a Berek variable wave plate (New Focus). When needed, a second polarizer was placed after the variable wave plate, allowing the excitation light to be linearly polarized in any desired plane. The excitation light was then focused onto the sample using a 60 \times , 1.4 NA oil immersion objective lens. The emitted fluorescence was collected by the same objective, passed through a band-pass filter (Omega Optical) to attenuate residual excitation light and directed onto a

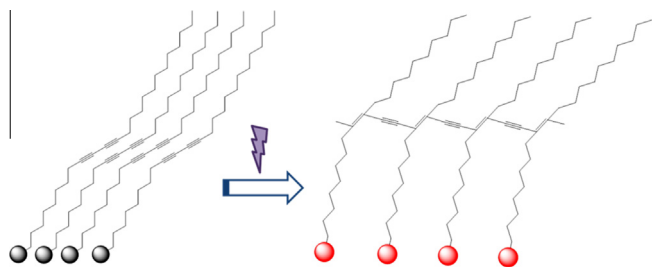


Fig. 1. Schematic illustration of photopolymerization process of 10,12 pentacosadiynoic acid films, and the resulting photopolymer film structure.

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