

Optical Microscopy of Polycrystalline Oligo(phenylenevinylene) Films

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Abstract

Laser scanning confocal microscopy (LSCM) has been used to characterize the emission properties of polycrystalline films of a phenylenevinylene oligomer. The emission profiles obtained from different crystalline regions are distinct and indicate that different molecular environments exist within the films. The spectra obtained from polycrystalline films contain a broad low energy component that is not observed in non-crystalline oligomer samples, and is consistent with excimer emission.

Keywords: photoluminescence, PPV, conjugated oligomers

1. Introduction

Oligophenylenevinylenes (OPVs) have been widely studied as model compounds for PPV and other related compounds. Both optical and quantum chemical studies have investigated the electronic structure and transitions of these oligomers.^{1–5} Because OPV molecules are smaller and less complicated than PPV, they are much easier to model computationally. Because OPVs are well-defined, they allow researchers to control and define the parameters that they are studying, such as the effect of increasing conjugation length. By investigating both the nature and evolution of photoexcitations in the well-defined oligomer, researchers can establish structure–property relationship trends, and use these findings to estimate the properties of the more complex polymer.

Recent works have described the synthesis and electroluminescence properties of a tetrahedral OPV molecule. The tetrahedral OPV is comprised of four 6-phenyl oligomers bound to a central sp³-hybridized carbon.^{6,7} The “arm” oligomer was synthesized for comparison. In particular, the tetrahedral molecule was designed with a geometry to discourage molecular packing. The arm molecule, by contrast, is shown to form intricate polycrystalline structures.

2. Experimental

Films of 4-((2',5'-dioctyloxy-4'-styryl)styryl)styryl)stilbenylmethane (**6ROC₈H₁₇**) were spin-cast onto quartz substrates. Film thickness was controlled by spin frequency and solution concentration. Annealed films were prepared by heating the sample to the glass transition temperature (140 °C), then slowly cooling (0.5 °C/min) to room temperature.

All sample preparations were performed in a nitrogen-filled glove box.

The films were studied by both conventional fluorescence microscopy and laser scanning confocal microscopy (LSCM). We use a home-built microscope for all LSCM measurements. The details of the LSCM setup have been described elsewhere.⁸ A Xe arc lamp (75 W) filtered for either blue (400–490 nm) or green (515–560 nm) light was used as the excitation source for the fluorescence microscope. The microscope was operated in reflectance mode and was fitted with a 10x/0.4 numerical aperture (NA) microscope objective (power ~ 3W/cm²). Photographs of the fluorescence images were taken using a standard telephoto camera fitted to the eyepiece of the microscope.

3. Results

The fluorescence micrograph in Figure 1 shows the fluorescence from an annealed polycrystalline film of **6ROC₈H₁₇**. Using LSCM, we were able to “zoom in” on various regions of the film and obtain spatially resolved spectra.

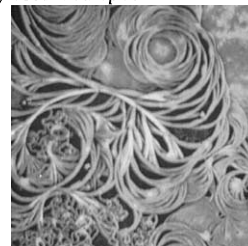


Figure 1. Fluorescence micrograph of a polycrystalline **6ROC₈H₁₇** film.

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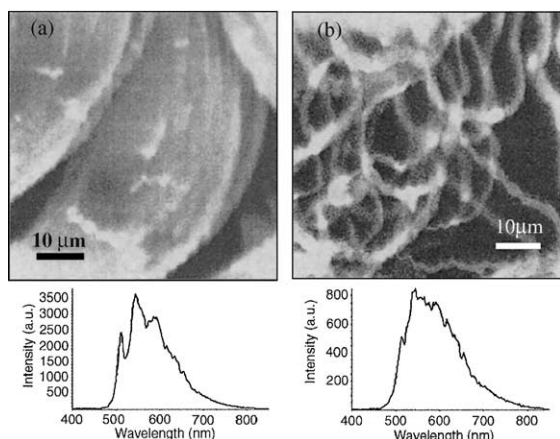


Figure 2: a) LSCM image of a sheet-like crystalline region of a $6\text{ROC}_8\text{H}_{17}$ annealed film. The spectrum below was obtained from the center of the image. b) LSCM image of a ribbon-like crystalline region of a $6\text{ROC}_8\text{H}_{17}$ annealed film. The spectrum below was obtained from the lower right-hand corner of the image.

Figure 2a and 2b are examples of images obtained by LSCM, with corresponding spectra. We see that spectra obtained from each different regions of the film vary in spectral profile depending on local environment. Two major crystalline domains occurred in the annealed $6\text{ROC}_8\text{H}_{17}$ films. The majority (>80%) of the surface of the glass was covered with ribbon-like structures such as the ones seen in the LSCM image in Figure 2a. The rest of the film was comprised of several large (>1 mm²) regions containing sheet-like crystal formations (Figure 2b). Vibronic structure usually occurred in the spectra obtained from bright, sheet-like crystalline regions of the film. The ribbon-like structures of the film tended to have broad, featureless spectra that lacked vibronic structure. We hypothesize that the lack of structure on the ribbon-like crystal spectra indicates that these regions are less ordered than the sheet crystalline regions. Homogenous broadening due to a number of different molecular environments may wash out the vibronic structure in the ribbon-like regions, while the sheet crystalline regions contain more uniform molecular environments allowing the vibronic peaks to be resolved. Polarization studies on the two types of crystalline regions revealed a marked anisotropy, indicating that the electric dipoles of the molecules are aligned parallel to one another. The anisotropy indicated that the molecules packed with their long axes parallel to the long axis of the crystalline features. This is consistent with the herringbone packing observed for similar compounds.^{2,3}

Films of $6\text{ROC}_8\text{H}_{17}$ were also prepared in which the sample was heated to its glass transition temperature, and then immediately immersed in liquid nitrogen to discourage crystal growth. The resulting “films” contained numerous islands of material surrounded by bare glass (Figure 3). The bright islands of the film were found to be completely isotropic with modulated laser polarization, indicating a lack of oriented molecular packing. The spectra from these islands were uniform and resembled the

solution spectrum of the bulk sample (Fig. 3b). It is interesting to note that the spectra taken from both the quenched films and solution are significantly narrower on the lower energy side of the spectrum than the spectra obtained from both domains of the crystalline films. Because the liquid nitrogen “quenching” process discourages molecular ordering, this result is not surprising. The formation of delocalized states among the closely packed oligomers in the crystalline films causes the increased low energy emission, often referred to as ‘excimer’ emission.⁹

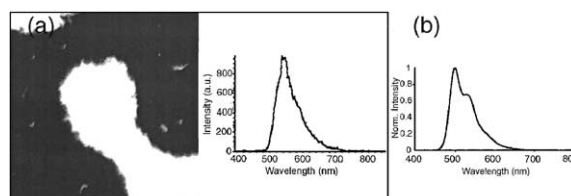


Figure 3: a) 100 μm LSCM image of a quenched $6\text{ROC}_8\text{H}_{17}$ film. A typical spectrum obtained from the bright regions of this sample is shown on the right. b) Chloroform solution spectrum of $6\text{ROC}_8\text{H}_{17}$.

4. Conclusions

We have shown LSCM is a useful tool in probing the mesoscale properties of conjugated organic films. Spectral differences between different regions of these films have been resolved with distances of less than 1 μm. We see evidence of excimer formation among highly ordered oligomers films, while randomly ordered oligomers retain a narrow emission spectrum in the solid state. The emission spectra of different crystalline regions reveal different spectral profiles which are indicative of the molecular environments within these regions.

5. References

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