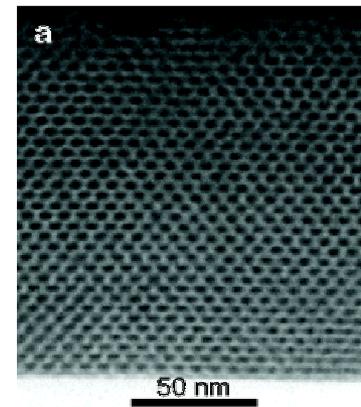


# Non-Linear Optical Properties of Aligned Conjugated Polymers

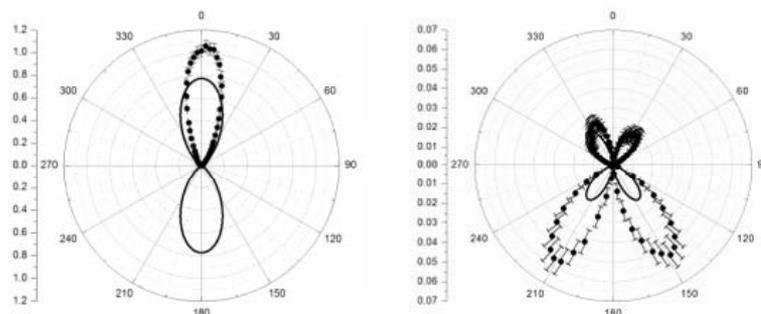
Benjamin J. Schwartz, UCLA (DMR-0305254)

- Conjugated polymers are plastic semiconductors with potential applications in flexible, large-area optoelectronic devices such as LEDs, displays, and solar cells. Our approach utilizes non-linear optical (NLO) spectroscopy to understand the properties of conjugated polymer/metal interfaces, e.g., chemical bonding, electronic doping, to understand and improve device performance.
- By encapsulating the polymer chains in a mesoporous silica framework, we can precisely measure all the NLO properties. Figure 1 shows a TEM image of the aligned MEH-PPV/silica composite material.<sup>1</sup> Figure 2 shows the the second harmonic (SHG) signal from the sample as a function of angle. The solid curves through the data points are fits to a model that uniquely determines the ratios between the different NLO tensor elements of the polymer. Our future plans are to use these elements to understand the interfaces in working polymer devices such as LEDs.

<sup>1</sup> Tolbert et al., JACS **126**, 4476 (2004).



**Figure 1:** TEM of an aligned honeycomb mesoporous silica-conjugated polymer composite<sup>1</sup>



**Figure 2:** Parallel-polarized (left) and cross-polarized (right) SHG signals as the direction of the polymer/silica composite sample is rotated.

Since all polymer-based optoelectronic devices require the use of metal electrodes, understanding the nature of conjugated polymer/metal interfaces is critical for understanding and improving device performance. When a metal is evaporated onto a conjugated polymer, carbon-carbon bonds might be broken, metal-carbon bonds might be formed, and the polymer might become electronically doped. Thus, the way charge is injected into polymer-based devices is determined by the details of the chemistry at the polymer/metal interface. Our approach takes advantage of surface-specific non-linear optical spectroscopies, second harmonic and sum frequency generation, to directly probe the chemical structure of conjugated polymer interfaces. Initial experiments are focused on polymer/vacuum interfaces, relating the non-linear optical signals with morphological information from AFM. Additional experiments explore the existence of metal-carbon bonds and the possibility of doping of the polymer at polymer/metal interfaces. Interfacial carrier dynamics will also be probed in operating devices, allowing device performance to be correlated with specific changes in the polymer/metal interfacial structure. The overall goal is to relate interfacial properties and morphology with device performance, so that the interfaces can be optimized for desired applications.

For the past year, our group has been using second harmonic generation (SHG) to understand the properties of polymer/metal interfaces. Interpretation of our data requires the values of the second-order non-linear susceptibility tensor of MEH-PPV. In order to measure this tensor, we have obtained a sample of individual MEH-PPV chains embedded into aligned silica nanopores through a collaboration with Sarah Tolbert's group here at UCLA.[1] The aligned polymer composite sample provides a unique opportunity to measure the non-linear optical properties of individual polymer chains. Unlike a solution-cast film, where the polymer chains are randomly oriented, the polymer chains in the pores are electrically separated from each other and arrayed in a regular lattice, making determination of the molecular symmetry, an important consideration in SHG spectroscopy, tractable. In addition, the alignment of the chains in the composite means that the sample is non-centrosymmetric, making SHG signal possible from the bulk rather than just from the interfaces.

We have recently completed a preliminary series of SHG measurements on the aligned polymer/pore composite samples. The samples were mounted on a rotation stage and oriented normal to a laser beam with the pores initially aligned with the laser polarization. Light pulses with  $\sim 120$ -fs duration were used to provide the intensity needed for efficient SHG; the pulses were tuned to 1000 nm to take advantage of resonance enhancement with the peak absorbance of the polymer at 500 nm. The fundamental was blocked with a filter, and the SHG signal passed through a polarizer set either parallel or perpendicular to the incident light and was detected with a PMT. All signals were referenced to the SHG from a piece of *z*-cut quartz to normalize out any fluctuations in the laser intensity.

The first set of data, taken as the polymer composite sample was rotated around the laser beam axis, is shown in Figure 2. The data were fit to a simple model assuming  $C_{\infty v}$  the polymer chains (i.e. that the chains are axially symmetric, but with no perpendicular mirror plane). This is the symmetry expected from taking an object with  $C_s$  symmetry (which is the correct symmetry for an MEH-PPV chromophore based on its chemical structure) and rotationally averaging it around the pore axis. This model was globally fit to both sets of data and reproduces both the functional form and relative magnitude of the signals using only a single adjustable parameter. The deviation in magnitude from the model of the cross-polarized data between 90 and 270 degrees is most likely due to non-uniformity in the film. We note that it is not possible to treat the polymer as a rigid rod ( $D_{\infty h}$  symmetry), since this would yield zero SHG signal due to the presence of an inversion center. The fact that the signal is well fit with  $C_{\infty v}$  symmetry indicates that the polymers are not orientationally isotropic within the pores, but rather have a preferred direction (at least over a domain comparable to the laser spot size of 500  $\mu\text{m}$ ).

As we improve our angular resolution, the data above should allow us to fit all the unique tensor elements of the second-order hyperpolarizability of MEH-PPV. Once we have determined these elements, we plan to explore the properties of the polymer/metal interfaces in working devices.

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**Education:** This project has provided training in the use of femtosecond lasers, non-linear optics and semiconductor devices physics for three students (one of whom is of Latino descent and one of whom is female). An undergraduate student (Sean Roberts, not pictured) also has worked on the project.



From left to right: Betsy Raymond, Ian Craig and Ignacio Martini

**Broader Impacts:** Since any device fabricated from conjugated polymers requires metal electrodes in contact with the polymer, understanding the polymer/metal interface is critical to exploiting these materials to their maximum potential in applications. For example, how are polymer-on-metal interfaces (created by spin-coating the polymer onto a metal) different from metal-on-polymer interfaces (created by thermal evaporation of the metal onto the polymer)? The NLO studies underway in our group will provide a molecular-level picture of the properties of polymer-metal interfaces, hopefully paving the way to more efficient commercial devices based on these materials.