

# Basic Studies in Vibrational Excitation of Polymer Surface Photochemistry and Rapid Thermal Processing

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Things made from polymers are everywhere in modern life and their importance will only grow. Unfortunately basic scientific attention has been distressingly uneven and the resulting gaps in fundamental understanding are key barrier to needed progress in applications. Fortunately a confluence of several elements creates now a unique opportunity for research to now move forward.

The application needs chiefly depend on surface effects in the final article, but fundamental understanding is greatest at the other end: the chemistry of polymer synthesis. The greatest factor causing change is the availability of in recent years of light sources that can drive surface photochemistry and rapid thermal processing. First came deep UV excimer lasers and now excimer lamps that can access high cross-section electronic transitions. A parallel advance is taking place now for driving vibrational transitions. It includes tunable, high peak power laboratory systems for molecular studies and now, largely through DoE's efforts, an FEL that further has enough average power to produce sufficient quantities of materials for subsequent studies.

A second major change factor is the power and accessability of computational modeling. All aspects of the problem can be represented, at least for reasonably large molecular model compounds if not for whole polymers. The models yield great detail, so that researchers can focus experiments and interpret results incisively. Computational modeling also points the way to experimental modeling, indicating where well-defined molecular species have the best prospect of serving as proxies for unavoidably complex whole polymers. Already some success is evident.

We intend to address three sets of issues, in the present phase for vibrationally-driven transitions. They are the nature of the vibrational excitation process, the subsequent intramolecular flow of energy, and the intermolecular energy transport. What is learned about the molecular-scale events needs to then be related to the resulting materials properties.

Our experiments will address nylon and PET, because they are used so widely, they are strongly responsive to electronic and vibrational excitation, and so much work has already been done in the UV. We have defined and prepared molecular model compounds for nylon and are doing so for PET. We have calculated absorption spectra and collected some of them. A new two-color, tunable femtosecond infrared laser facility at the University of Virginia offers the opportunity to directly observe the molecular events. The closely similar capabilities of the Jefferson Lab IR FEL (except for power (10 mW vs. 1 kW) and repetition rate (1 kHz vs. 10 MHz)) will utilize what is learned to produce enough material to investigate the properties. We will do the RTP experiments on the FEL directly, since they require both tunability and high average power. We have already calculated operating parameters based on what has already been learned in the UV with excimer lasers. Finally, the FEL has a recognized potential to be developed into a commercially viable light source technology for practical applications that may emerge from what is found.