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Modeling the Dehydrochlorination of PVC using LD-FT-ICR MS

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**CHEMISTRY: INORGANIC, PHYSICAL, &
ANALYTICAL**

**51. Modeling the Dehydrochlorination of PVC
using LD-FT-ICR MS**

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With the advent of new polymer technology, many different types of plastics and plastic additives are being produced. These new types of additives and plastics make the recycling of polymers increasingly difficult. Pyrolysis is a recycling technique that allows for the thermal degradation of polymers and the retrieval of many different hydrocarbons. Pyrolysis is utilized to thermally degrade organic compounds and retrieve economically viable products from difficult to recycle starting materials. Since pyrolysis is based on thermal decomposition, the products that are produced are dependent on the amount of thermal energy that is allowed into the system. With the difficulty in knowing what hydrocarbons are going to be produced from the different types of plastics, a cost effective way to screen polymers rapidly needs to be developed.

Current techniques involve the use of pyrolysis-gas chromatography/mass spectrometry (py-GC/MS) and laser desorption time of flight mass spectrometry. These techniques allow analysis of the products but fail to give in-depth mechanistic details. Laser desorption Fourier transform ion cyclotron resonance mass spectrometry (LD-FT-ICR MS) allows for modeling of the chemistry associated with pyrolysis in a cost effective manner. This project provided a unique approach to changing the products formed, by optimizing the pyrolysis conditions (temperature and catalysts). Initial comparisons of data obtained using the LD-FT-ICR MS approach were compared to data obtained from thermal decomposition in a benchtop vacuum pyrolysis reactor. The good correlation indicated that the process can be modeled in the gas phase. One of the primary steps in the pyrolysis of poly(vinyl chloride) is the dehydrohalogenation reaction. The energetics of this reaction were studied both theoretically and empirically. Gas phase modeling in the presence of iron indicates that metals ions can act as a catalyst for the reaction.

**52. RAIRS and TPD studies of the direct
photopolymerization of thin films under ultrahigh
vacuum conditions**

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The photoinduced polymerization of cyclic monomers adsorbed on Ag(110) has been studied using a combination of reflectance absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). The ultimate goal of this research is to form ordered thin polymeric films.

Styrene polymerizes upon ultraviolet irradiation. Post-irradiation TPD results indicate the formation of several species in the film, identified as dimer, trimer and tetramer. RAIRS data recorded as a function of temperature provide evidence for the formation of polystyrene. A mechanism for this reaction is proposed. Experiments are currently being performed using 1-vinyl-2-pyrrolidinone and aniline. The results of these studies will be presented and discussed.

**53. Chemiluminescent flow injection
measurement of glutamate in the presence of
interference**

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A flow injection chemiluminescent system has been developed for measuring micromolar concentrations of glutamate in synaptic vesicle samples, where the presence of glutamate is due to its role as a neurotransmitter. The analysis is achieved through the oxidative conversion of glutamate to hydrogen peroxide via glutamate oxidase. The signal is then generated by reaction of hydrogen peroxide with the chemiluminescent reagent lucigenin. The importance of this system is the ability to measure the concentration in the presence of interfering compounds such as ascorbic acid.

The system requires two parallel paths for the sample. The first path includes a glutamate oxidase reactor and the corresponding signal represents light produced from glutamate and endogenous interferences. A blank reactor is placed in the second path and the resulting signal corresponds to only the interferences. Subtraction of the two signals corresponds to a chemiluminescent intensity representative of only glutamate.

Calibration experiments illustrate a linear response to glutamate from 0-100 μ M with a detection limit of 1 μ M and a throughput of 80 samples per hour. A blind validation study demonstrates the ability to measure glutamate accurately in the absence of