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Modeling PVC Pyrolysis Using Laser Desorption Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Introduction

Thermosets and thermoplastic production has been increasing at an average rate of 5% annually. The request for plastics is on the rise due to increasing demands for business machine housings, building and construction demands, and increasing automotive sales. The United States alone produced 75.3 billion pounds of plastics in 1994, a 9% increase over 1993.¹ With new types of plastics being developed such as the new generation of polyolefins based on metallocene catalysts technology, new and innovative techniques for recycling of these plastics will also need to be developed. Thermoplastics can be remelted after it has been molded so it can be recycled by re Injection molding techniques. In contrast, thermoset plastics cannot be softened again or dissolved once molded, making reuse/recycling difficult if not impossible.

An innovative way to recycle thermoset plastics is through pyrolysis. Pyrolysis is thermal degradation of organic starting materials in the absence of oxygen. This can occur in either a vacuum or under an atmosphere absent of oxygen. The thermally degraded product can be collected and utilized as a liquid feedstock for subsequent cracking and fractionation by an oil refinery or if one product is produced in a high quantity it can be collected and distilled to remove any minor products. 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. So if the pyrolytic environment is changed the products that are formed will be different.

One instrument that allows the analysis of gas phase reactions and the ability to study the molecular ion and its fragments is Fourier transform ion cyclotron mass spectrometry. With the use of pulsed laser heating, samples can be subjected to a very large and rapid temperature increase which stimulates pyrolytic conditions. When coupled with laser desorption, FT-ICR MS allows the study of reaction mechanisms during thermal decomposition.

Experimental

Samples used in this study consisted of poly(vinyl chloride) shredded into 8-10 mm pieces. The shredded PVC was then placed inside a quartz tube that was connected to a bench scale pyrolysis reactor. The system was evacuated to 1×10^{-3} torr utilizing a Welch Model 8905 vacuum pump. The PVC was heated by a Lindberg tube furnace oven to a temperature of 250° C to allow for the low temperature dehydrochlorination reaction to occur. The gaseous products were collected by a cold trap that was part of the pyrolysis apparatus. The cold trap was removed and the products were allowed to go back into the gas phase. The gaseous products were collected and analyzed an IonSpec OMEGA 50 Fourier transform ion cyclotron resonance mass spectrometer with a high field Walker Scientific electromagnet held at 1.03 by a Balzer J30 liter/second turbo molecular pump backed by an Alcatel direct drive roughing pump. Gaseous products were set and maintained using a Varian leak valve. Experimental pressures ranging from 2×10^{-7} - 3×10^{-7} torr in a 5 cubic centimeter analyzer cell were measured using a Bayard-Alpert type ionization gauge. The gaseous samples were continuously ionized by an electron beam at an electron energy of 60-70 eV. The filament current ranged from 1.0-1.4 microamps. Data was collected using the IonSpec 50 data system.

Following the low temperature dehydrochlorination the pyrolysis reactor was evacuated to remove any left over gaseous products that were formed from the initial thermal degradation. The resulting polymer residue was further reduced at a temperature of 750° C to allow for the high temperature degradation to occur. The gaseous products were collected and analyzed as previously described.

To analyze the reaction mechanism utilizing LD-FT-ICR MS the sample was attached to the solid insertion probe of the FT-ICR and inserted into the IonSpec OMEGA 50 FT-ICR for analysis. Background pressure was maintained at 6.9×10^{-7} torr. The sample was ionized by a Continuum MiniIle Nd:YAG laser. The operating frequency of the laser was quadrupled to 266 nm with a pulse width of 4

nanoseconds. The repetition rate of the laser was controlled by the FT-ICR interface program at a maximum rate of 10 Hz. The energy of the laser output was 20 mJ with a peak power of 0.5 MW which results in thermal degradation/desorption and ionization to occur. The laser desorption ionization was triggered by the FT-ICR and the ions were detected following a 90 millisecond delay to permit stabilization of the desorbed ions and to maintain the maximum laser repetition rate.

Results and Discussion

Based on the spectrum obtained during pyrolysis at the low temperature dehydrochlorination reaction, the major product produced was HCl. The high temperature reaction underwent an aromatization with the major product being benzene. Shown in Figure 1 is the negative ion LD-FT-ICR MS of PVC. This spectrum illustrates both the dehydrochlorination reaction along with the aromatization reaction occur.

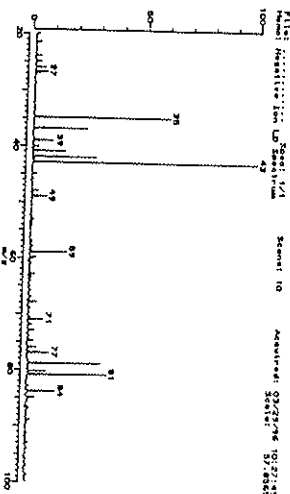


Figure 1
Negative ion LD-FT-ICR MS Spectrum

The above results show the positive ion does not undergo gas phase reactions. The results of the negative ion suggest that the aromatization reaction occurs as a condensed phase reaction (Figure 2).

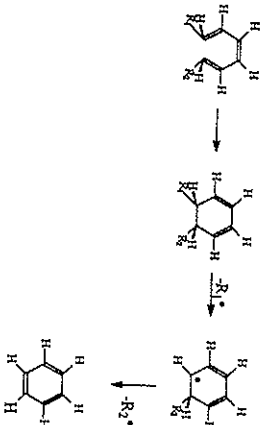


Figure 2
Aromatization reaction of PVC by LD-FT-ICR MS

Following the dehydrochlorination reaction the resulting polyene undergoes an aromatization reaction with benzene being the major product formed.

¹ Reisch, M.S. C&E News, 1995, p.30.