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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

CATALYTIC CRACKING OF POLY(ETHYLENE) AND POLY(STYRENE) BY
SILICA-ALUMINA, HZSM-5 ZEOLITE AND SULFATED ZIRCONIA

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
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degree of
DOCTOR OF PHILOSOPHY

BY
RONG LIN
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CATALYTIC CRACKING OF POLY(ETHYLENE) AND POLY(STYRENE) BY
SILICA-ALUMINA, HZSM-5 ZEOLITE AND SULFATED ZIRCONIA

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DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY

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Rong Lin

ABSTRACT

Communities in the United States are in dire need of alternatives to municipal solid waste landfilling. Of the solid waste components currently placed into landfills, plastics are particularly undesirable because of their limited biodegradability. This work was carried out to investigate the potential use of catalytic cracking to convert plastic wastes into mixtures of useful chemicals. The effects of silica-alumina, HZSM-5 zeolite and sulfated zirconia cracking catalysts on the thermal degradations of poly(ethylene) and poly(styrene), which constitute nearly 80% of plastic packaging in the United States, are described.

The catalytic cracking mechanisms of poly(ethylene) and poly(styrene) differ considerably from their thermal cracking mechanisms. In the case of poly(ethylene), thermal cracking leads to the formation of a wide range of hydrocarbon products. As a result, recycling methods for poly(ethylene) based on thermal cracking are of limited use. However, the molecular weight range of poly(ethylene) volatile decomposition products obtained when silica-alumina, HZSM-5 and sulfated zirconia catalysts are present is narrower than that obtained by thermal cracking. Catalysts
dramatically change the volatile products obtained by heating poly(styrene). Whereas styrene is the most abundant volatile product resulting from neat poly(styrene) thermal cracking, benzene is the most abundant product when poly(styrene) is catalytically cracked. For both poly(ethylene) and poly(styrene), catalytic cracking product distributions depend on the choice of catalyst. The thermal stabilities of poly(ethylene) and poly(styrene) also depend on their initial molecular weights. Overall volatilization activation energies for poly(ethylene) and poly(styrene) thermal decompositions are considerably reduced by the presence of cracking catalysts and the magnitude of the reduction depends directly on the catalyst acidity. A lowering of overall volatilization activation energies by cracking catalysts is desired for polymer recycling applications because it greatly reduces the cracking temperature required to decompose plastic wastes, which reduces the operational costs of the process.
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Chapter I

Introduction

1.1 Municipal Solid Waste and Plastic Wastes

Municipal solid waste, an inevitable by-product of human activity and endeavor, refers to residential, commercial, institutional and industrial solid waste\textsuperscript{[1,2]}. Examples of municipal solid waste (MSW) include what we throw away each day, such as: food, newspapers, yard waste, old appliances, household garbage, and anything else that ends up in the garbage or trash.

The amount of MSW generated annually in America has been rising steadily from 88 million tons in 1960 to over 207 million tons in 1993\textsuperscript{[3]}. If current trends continue, the amount of MSW generated is expected to reach 222 million tons per year by the year 2000\textsuperscript{[2]}. During the past decade, MSW has become more and more of a social and environmental concern around the world. The "four R's" of waste management (reduction, reuse, recycling and recovery)\textsuperscript{[1,4]} are well known to most people. Reduction includes activities by both manufacturers and consumers to avoid unnecessary waste generation. Reuse means using objects or materials again. Recycling is using waste materials in place of virgin materials to make useful
products. Recovery refers to processes of extracting energy from waste.

Despite increases in the amount of waste reused, recycled and recovered, more than 70% of all MSW in the United States is placed into landfills. About 13% of MSW is recycled and about 14% is incinerated (Figure I.1)\(^5\). Landfilling is generally the least expensive method of MSW management. Due to the disproportionate amount of waste going to landfills, many landfills have been closed in recent years or are scheduled to be closed because they have reached their designed capacity. In fact, the total number of landfills has declined from over 18,000 in 1960 to about 5,000 in 1992\(^6,7\). By the year 2000, the number of landfills in operation is projected to drop to about 1,800\(^2\). Research conducted by the National Solid Waste Management Association in 1992 revealed that the currently permitted landfilling capacities of 27 states will be exhausted by the year 2000\(^8\). The decrease in the number of landfilling sites is creating an acute shortage of landfilling space and is also causing waste to be transported over longer distances. Establishing new landfills is difficult due to new regulations adopted to address the concerns of local residents for their environment. Concerned citizens who become fearful of proposed landfills in their community adopt a "Not in My Back Yard" attitude\(^1,4\). Stringent environmental requirements for landfills are being enforced by states and local governments. The EPA's 1991 regulations prohibit the development of landfills within floodplains, fault zones, wetlands, seismically active regions, and unstable areas national-wide\(^1,6\). As a result, the latest trend in U.S. sanitary landfill practices has been to build fewer but larger solid waste disposal
Figure 1.1 Municipal solid waste management in 1990.
However, this can result in very long hauling distances, which raises landfilling costs. In addition, under the new regulations, owners and operators of landfills are responsible for required groundwater and soil monitoring and other follow-up activities for 30 years following the closure of a landfill\textsuperscript{[6,10]}. As a result, landfilling will almost certainly be reserved for only the most intractable solid wastes in the very near future\textsuperscript{[11]}. Clearly, new waste treatment processes that reduce the volume of solids that must be landfilled are urgently needed.

Waste-to-energy (WTE) incineration is a common method to reduce the volume of MSW placed in landfills. In this method, MSW is burned to produce energy. The energy stored in one ton of MSW is equivalent to the energy generated by 500 kg of coal\textsuperscript{[12]}. It was estimated that more than 16% of the MSW in the United States was incinerated in 1990 and the percentage is still increasing\textsuperscript{[13]}. If MSW is incinerated in a well-designed and carefully controlled WTE plant, incineration can reduce MSW by 80% by weight and 90% by volume\textsuperscript{[14]}. Although incineration facilities are equipped with air pollution control devices, incineration has become an unpopular option for disposing of MSW because of environmental issues such as the release of highly toxic organic materials (e.g. dioxins) and heavy metals (e.g. Hg) that are found in incineration plant stack gases\textsuperscript{[12,15,16]}. In addition, incineration generates fly ash, which contains high concentrations of heavy metals, such as Hg and Pb\textsuperscript{[15]}. The public is opposed to incineration because of potential health risks from toxic byproducts. As a result, more environmentally-friendly waste treatment processes are being sought.
Among solid wastes, plastic wastes have received a lot of attention for recycling because of their substantial volume due to their low densities. As reported by the U.S. EPA\textsuperscript{2}, MSW produced in the United States in 1990 consisted of 38\% by weight paper, 18\% yard waste, 9\% plastics, and glass, metals and food wastes ranged between 6\% to 8\% each. By volume, paper was the largest component of MSW (32\%). However, plastics ranked second in volume, representing 21\% of the total MSW volume (Figure 1.2). Plastics have become widely used materials in the United States since the middle of the 1970's and the plastics manufacturing industry has grown larger than the steel and aluminum industries combined\textsuperscript{15}. The three major markets for plastics are: packaging (39\%), construction (27\%), and transportation (11\%). Other applications of plastics include electrical and electronic uses, housewares, agricultural applications, furniture and furnishings. There are four commodity plastics that constitute 71\% of the world's plastics production. They are: poly(ethylene) (PE), poly(propylene) (PP), poly(styrene) (PS), and poly(vinyl chloride) (PVC) (Figure 1.3). These plastics are commonly found in MSW in the form of bottles and containers, or as packaging and wrapping films. In 1990, about 14.8 billion pounds of plastics were used for packaging purposes. Four billion pounds were used for containers and 2.2 billion pounds were used specifically for beverage containers\textsuperscript{15}. World plastics production is expected to increase 3.7\% annually\textsuperscript{17}. Solutions have to be found for better recycling of the ever increasing quantities of plastic waste so that it is not placed in landfills.
Figure 1.2 Material discards in MSW by volume in 1990.
Figure 1.3 World plastic production in 1994.
1.2 Plastic Waste Treatment

Because of the tremendous growth in the use of plastics, especially for short-term packaging, increased attention has been focused on its reuse, recycling and recovery. The American Society for Testing and Materials (ASTM) has defined four different types of plastics recycling methods:

1. **Primary recycling** - "the conversion of scrap plastics by standard processing methods into products having performance characteristics equivalent to the original products made from virgin feedstocks".

2. **Secondary recycling** - "the conversion of scrap or waste plastics by one or a combination of process operations into products having less demanding performance requirements than the original material".

3. **Tertiary recycling** - "the process technologies for producing chemicals and fuels from scrap or plastic wastes".

4. **Quaternary recycling** - "the process technologies for recovering energy from scrap or plastic wastes by incineration".

Primary recycling has been used by the plastics industry for many years. Plastics scrap generated in manufacturing processes are often clean and consist of a single type of plastic. They can be easily remelted, pelletized, and reused without reducing the product quality. However, most plastic wastes are contaminated with impurities and consist of mixed plastics and primary recycling cannot be used. Secondary recycling can be used for homopolymer plastic wastes that contain
impurities to produce new valuable, but less demanding in performance, plastic products. In order to employ secondary recycling, a means for sorting and separating plastic wastes is required. In addition, because typical plastic melting temperatures are not high enough to destroy all harmful contaminants, the U.S. Food and Drug Administration has banned the use of recycled plastics for products that come in direct contact with food. Tertiary recycling can be used to convert contaminated and mixed plastics into basic chemicals and fuels. Unlike primary and secondary recycling, tertiary recycling can be applied to commingled plastics and plastics that contain additives, fillers, and colorants, which makes prior separation of plastic wastes unnecessary. Waste-to-energy (WTE) techniques constitute quaternary recycling. Plastics are an abundant source of energy. For example, polyolefins, which constitute almost 90% of plastic wastes, typically have calorific values greater than 20,000 Btu/lb, which is almost twice that of coal\textsuperscript{[18]}. However, solid waste that contains large amounts of plastics is unsuitable for WTE incineration because the high exothermicity of plastic combustion causes incinerator temperatures to rise above maximum operating temperatures\textsuperscript{[18]}.

### I.3 Catalytic Cracking of Plastic Wastes to Hydrocarbons

Because plastics have high energy contents, it may be advantageous to convert plastic wastes to fuel. The economic benefit of producing a high quality hydrocarbon fuel from plastic waste can be illustrated by way of an example.
According to 1990 statistics, on average, each U.S. citizen generates about 0.36 pounds of plastic waste per day\textsuperscript{[19]}. On average, in a community of 100,000 people, 36,000 pounds of plastic wastes are collected each day. Assuming that the processes used to separate plastic waste from other municipal waste components are only 80% efficient, 28,800 pounds of plastic waste would be available for refuse-derived fuel production each day. If only 65% of the recovered plastic waste is converted to a high quality liquid fuel (65% conversion of plastic waste to fuel oil has already been achieved\textsuperscript{[20]}), 3,270 gallons could be produced each day. Because a high quality plastic waste derived liquid fuel could substitute or be blended with motor fuel, it might be used to power municipal vehicles and machinery. Over the span of a year, almost 1.2 million gallons of fuel could be produced. At a value of $1/gallon, this fuel would be worth $1.2 million to the community. This financial benefit is greater than what would be gained if all of the recovered plastic waste was recycled by currently available processes (assuming a $200/ton\textsuperscript{[21]} value for recycled plastic).

Because it can be applied to contaminated commingled plastics, tertiary recycling is considered the most promising of the recycling methods proposed so far for reducing the amounts of plastic wastes placed into landfills\textsuperscript{[22]}. The typical plastic waste tertiary recycling method consists of pyrolysis of the plastics followed by catalytic reforming of the volatile pyrolysis products. Pyrolysis has been used to convert plastics wastes and tires into chemicals since the 1970's\textsuperscript{[15,23]}. Non-oxidative pyrolysis of plastic wastes results in monomers, low molecular weight polymers, and
hydrocarbon mixtures with compositions that vary with temperature, pressure and the residence time in the pyrolyzer heated zone. The pyrolysis product mixture is sent to a refinery for further processing to produce: heating oil, gasoline, jet fuel, chemicals and plastics feedstocks\textsuperscript{[24]}.

Sinn et al\textsuperscript{[23]} found that pyrolysis of plastic wastes and scrap tires at 600 to 800 °C yielded up to 40% by weight aromatic compounds in a fluidized sand bed. Pilot-plant pyrolysis studies of mixed household wastes containing plastics have also been reported\textsuperscript{[15]}. A mixture containing 67.6% polyolefins, 1.7% PVC, 1.0% PS, and the remainder consisting of paper, metals, and sand etc, was pyrolyzed at 717 °C and yielded methane, ethylene, benzene, toluene, and carbon black as the main products. Conrad industries (Chehalis, WA) demonstrated the feasibility of using an existing tire recycling process to recycle post-consumer plastics at 500 to 600 °C\textsuperscript{[25]}. The Conrad process produced naphtha and gas-oil-range products in an 80% yield. Pyrogas, which can be used as a substitute for natural gas, comprised 17% of the products. One-third of the pyrogas was recycled back into the system and combusted to generate heat for pyrolysis, two-thirds of it was collected for sale. Conrad found that properties of the products depended on the feedstock. For example, neat poly(styrene) yielded 50% styrene. In general, pyrolysis reactions involved radical processes that resulted in complicated product mixtures that contained mainly olefins. Olefin products may oxidize or polymerize during storage, which reduces their commercial value. In most cases, high temperatures (above 700 °C) were required to produce pyrolysis product mixtures that had simple compositions.
Research has also been conducted to investigate the conversion of plastic waste to useful products by catalytic cracking processes. Compared to pyrolysis, catalytic processes typically yield mixtures with fewer products consisting of smaller hydrocarbons. Catalytic reforming is typically achieved by coupling a pyrolysis chamber to a catalytic reactor. Plastic waste is melted in the pyrolysis chamber, and then pyrolyzed at temperatures of 400-500 °C. Pyrolysis products are then fed directly into a second reaction zone that is filled with catalyst to reform pyrolysis products into useful mixtures, such as gasoline. Studies involving catalytic reforming of plastic waste pyrolysis products have been conducted by Fuji in Japan. In their process, plastics were melt extruded, liquified at 200 to 300 °C, and then thermally cracked at 400 °C. The resulting pyrogas was then passed over a ZSM-5 zeolite catalyst bed to produce a mixture of gasoline (25%), kerosene (25%), and gas oil (25%) in 80% overall yield. The recovery of indane derivatives from waste poly(styrene) plastics was demonstrated by Ogawa et al. Poly(styrene) was first thermally decomposed at 420 °C, then the thermal decomposition products were reformed in a catalytic reactor at 300 °C using silica-alumina as a cracking catalyst. The major products were reportedly ethyl benzene (18.3%) and styrene (10.1%). Indane derivatives that were produced by this process were 1-methyl-3-phenylindane, 1-methyl-1-phenylindane, and 1-phenylindane. The yields of these indane derivatives were about 20% of the weight of the liquid products recovered. In an experiment conducted by Ueno et al, styrene was recovered in over 70% yield from the catalytic degradation of thermally decomposed poly(styrene) at 350
Solid acids (e.g. Si-Al, HZSM-5), bases (e.g. BaO, CaO, MgO, K₂O) and some transition metal oxides (e.g. TiO₂, Cr₂O₃, Fe₂O₃, Co₃O₄, CuO and ZnO) were used as cracking catalysts. BaO was found to be the most active catalyst for the poly(styrene) degradation and gave the highest yield of styrene monomer and dimer (88%). Tertiary recycling of poly(ethylene) has been studied by several groups. In these studies, poly(ethylene) was first pyrolyzed at 450 - 500 °C, and then the thermally degraded products were fed into a catalyst bed at 400 °C. Silica-Alumina (Si-Al) and four zeolites: HZSM-5 with Si/Al ratios of 65 and 1000, HY, and rare earth metal exchanged Y-type zeolite (REY), were used as cracking catalysts. REY was found to be the best catalyst based on oil conversion, gasoline yield, and research octane number of the gasoline. Those authors concluded that the improved performance of the REY zeolite could be attributed to its stability, proper acidity, and relatively large pores into which large molecules could penetrate. In a later study, the authors chose four more REY zeolites with the same Si/Al ratio but different crystal sizes and acidities to crack a heavy oil derived from pyrolysis of PE. It was found that cracking reactions were favored by zeolites having small crystal sizes (0.1 µm). Increasing the number of acid sites on catalysts accelerated the cracking rates and yielded lighter hydrocarbons. The authors stated that an optimum acid site density was required to maximize both the gasoline yield and quality of the liquid products. It was found that the gasoline produced under the optimal conditions contained more isoparaffins and fewer aromatics than commercial gasoline, making it more environmentally favorable than commercial
Although some promising results have been obtained by using pyrolysis and pyrolysis followed by catalytic reforming for tertiary recycling of plastic wastes, the high energy cost of operating pyrolyzers and the fact that some products may oxidize or polymerize during storage and transportation make these processes currently impractical. Alternatively, direct catalytic cracking of plastic wastes at low temperatures may constitute a viable tertiary recycling method. Research has been carried out to study the effects of catalysts on polymer cracking product distributions\(^{35-40}\). It was found that the activation energies for PP, PE and PS decompositions were markedly lowered by the presence of catalysts\(^{36-38}\). Compared to processes involving pyrolysis, direct catalytic cracking results in a reduction in the energy required for processing plastic wastes (i.e. operational cost). For example, HY zeolite was found to reduce the onset temperature at which poly(ethylene) started to decompose by 200 °C\(^{37}\). Compared to pyrolysis, the molecular weight range of volatile products generated by heating polymer/catalyst mixtures were greatly reduced and the product distributions were found to depend on the catalyst used\(^{35-40}\). However, due to the high polymer/catalyst ratios used in most studies, it was impossible to identify primary cracking products because of secondary reactions between the volatile primary products and polymer residue.

Large scale plastic waste tertiary recycling must involve efficient and selective catalytic cracking of waste polymers. The development of waste polymer cracking processes will require detailed knowledge of the relationship between catalyst
properties and cracking product distributions. However, in order to study and compare the polymer cracking properties of different catalysts, it is preferable to examine the effects of catalysts without complications due to reactions of primary cracking products with polymer residue.

1.4 Project Description

The purpose of this project was to investigate the use of direct catalytic cracking to convert polymers commonly found in plastic wastes into useful hydrocarbon mixtures. The polymers studied in this project were poly(ethylene) and poly(styrene). These polymers were selected for study because they constitute nearly 80% of packaging applications in the United States. Thermal decomposition and catalytic cracking reactions of these polymers were compared. The catalysts used in this study included: amorphous silica-alumina, HZSM-5 zeolite, and sulfated zirconia (ZrO$_2$/SO$_4$). The effects of these catalysts on polymer cracking processes were investigated by comparing characteristic cracking temperatures and kinetic parameters. The effects of catalysts on the cracking product distributions were also investigated. Although the catalytic cracking of PE and PS was reported previously, those studies lacked detailed product analyses and no attempts were made to minimize secondary reactions between volatile products and polymer residue. Identification of the primary cracking products derived from PE and PS was a central focus of the project described here.
Polymer catalytic cracking processes for silica-alumina, HZSM-5 zeolite, and sulfated zirconia were compared by identifying the volatile products and semi-quantitatively determining their yields under various cracking conditions. Volatile cracking products were identified by using pyrolysis gas chromatography/mass spectrometry (pyrolysis GC/MS), thermogravimetry-mass spectrometry (TG-MS), and thermogravimetry-gas chromatography/mass spectrometry (TG-GC/MS). In these studies, secondary reactions were minimized by limiting the contact between primary volatile products and the polymer/catalyst mixtures by maintaining high catalyst to polymer ratios and providing rapid and efficient removal of volatile products after they were formed.
1.5 References


Chapter II
Instrumentation and Experimental Conditions

Pyrolysis gas chromatography/mass spectrometry (pyrolysis GC/MS), thermogravimetry-mass spectrometry (TG-MS), and thermogravimetry-gas chromatography/mass spectrometry (TG-GC/MS) were employed in this work to study polymer decomposition pathways. The apparatus used to conduct these analyses are described in the following sections. Data handling and other sample characterization techniques are also described in this chapter.

II.1 Pyrolysis Gas Chromatography/Mass Spectrometry

Pyrolysis gas chromatography/mass spectrometry was utilized to separate and characterize polymer decomposition and catalytic cracking products. The microfurnace pyrolyzer used for these studies was built in our laboratory\[1]. The microfurnace pyrolyzer components (Figure II.1) consisted of a 1.5 in. long, 1/4 in. o.d. stainless steel tube that was wrapped with Cotronics (Brooklyn, NY) ceramic tape. A coil of 1 mm thick nichrome wire was tightly wound around the ceramic
Figure II.1 Diagram of microfurnace pyrolyzer and sample probe.
tape as the heating element. The furnace was heated by passing current through the coil. The current was controlled by using a variac and the temperature was regulated by using a CN 76000 temperature controller (Omega Engineering Inc.).

A 40 mm long x 2 mm i.d. quartz tube was placed inside the stainless steel furnace to minimize contact of the volatile decomposition products with hot metal surfaces. The quartz tube was flared at the top to help guide the sample probe into the furnace during sample injections. Sample pyrolysis occurred within the quartz tube. At the top of the furnace was a 1/8 in. Ultratorr fitting (Cajon Co., OH), which served as the inlet for sample and thermocouple probes. Air leakage during probe insertion was minimized by the o-ring seal (without grease) in the Ultratorr fitting. A ball valve (Whitey Co., OH) connected the sample probe inlet and a stainless steel tee was used to isolate the probe inlet from the furnace and gas inlet. A 1/4 in. o.d. stainless steel tee connected the ball valve and the furnace and was used to introduce the GC column carrier gas. A Swagelok 1/4 in. to 1/16 in. stainless steel reducing union was welded to the bottom of the furnace and was used to couple the fused silica gas chromatographic column to the furnace. The column was inserted into the union until it was just inside the quartz tube. A graphite ferrule and a 1/16 in. stainless steel nut were used to seal the column to the union. All other connections were made with Swagelok fittings and stainless steel ferrules. The furnace was enclosed in two 2.25 in. x 1.5 in. x 0.85 in. ceramic blocks that served as insulation to provide uniform heating. The ceramic blocks were clamped together with stainless steel brackets and the assembly was mounted in place of a
standard injector on the top of a 5890 Hewlett-Packard (Palo Alto, CA) capillary gas chromatograph with the microfurnace pyrolyzer in a vertical position and the column connection located inside the GC oven.

An Omega QD-RT-K-18G-12 fast response thermocouple probe (Omega Engineering Inc., CT) was used to measure the microfurnace temperature. An adjustable collar on the temperature probe served as a physical stop so that the temperature of the furnace at the point at which samples were pyrolyzed could be measured. A temperature profile of the pyrolyzer microfurnace is shown in Figure II.2. The furnace temperature was set at 515 °C. The hottest position in the furnace is represented by the zero point in Figure II.2, and this point was 147 mm from the top of the Ultratorr fitting. The tip of the sample capillary tube, which was attached to the ceramic sample probe, was positioned to reach this point in the furnace by adjusting the sample probe collar so that the distance between the bottom of the collar and the probe tip was 147 mm.

The sample probe was a 6 in. long, 1/8 in. o.d. ceramic tube sealed and partially filled with ceramic cement. The sample was loaded into a glass capillary tube (90 mm long and 1.10 mm o.d.). The typical quantity of sample loaded into the glass capillary tube was about 0.2 mg. After tapping the powdered sample to the sealed end of the tube, the open end was sealed and drawn to a point by using a burner flame. With a glass cutter, a pin-hole was made in the pointed end of the tube so that volatile products evolved during sample pyrolysis could escape. The hole was made small enough so that sample powders did not fall out during
Figure II.2 Microfurnace pyrolyzer temperature profile.
pyrolysis. The sample probe was lightly tapped to compact the sample powder at the pin-hole end. The sealed end of the glass capillary tube was wrapped with teflon tape and was then inserted into the ceramic tube to achieve a tight fit (Figure II.3). Before injection, the sample probe was pushed through the Ultratorr fitting o-ring and just into the isolation valve. After allowing sufficient time to purge air that might have entered the microfurnace pyrolyzer when the isolation valve was opened, the sample probe was quickly pushed into the microfurnace until the collar reached the top of the Ultratorr fitting. This procedure caused the sample in the glass capillary tube to be rapidly heated, and volatile thermal decomposition products were swept by the He carrier gas onto the capillary GC column. The Ultratorr fitting o-ring seal and the positive pressure inside the microfurnace minimized air leakage during insertion of the sample probe into the furnace.

A 60 m x 0.25 mm DB-5 column with (5%-phenyl)-methylpoly(siloxane) as the stationary phase (0.32 μm film thickness) was used for all gas chromatographic separations. The helium carrier gas flow rate was 2 ml/min. For samples containing poly(ethylene), the GC oven temperature program consisted of a 2 minute isothermal period at -50 °C followed by a 5 °C/min ramp to 40 °C and a 10 °C/min ramp from 40 to 200 °C, and then another 10 minute isothermal period at 200 °C. For poly(styrene)/catalyst samples, the GC oven temperature program consisted of a 2 minute isothermal period at -50 °C followed by a 10 °C/min ramp to 280 °C, and then isothermal at 280 °C for 5 minutes. For neat poly(styrene), the same temperature ramp was used except that the 280 °C isothermal period was...
Figure II.3 Expanded view of the sample problem.
10 minutes instead of 5 minutes. All carrier gas flow rates were set and maintained by using a model 825 mass flow controller and a model 1605 controller unit (Edwards High Vacuum Inc., NY).

GC/MS detection of volatile products was achieved by directly connecting the fused silica capillary GC column to a Hewlett-Packard 5988 quadrupole mass spectrometer. The GC/MS interface was maintained at 200 °C. Electron impact mass spectra were obtained by using a 70 eV ionization potential and scanning from m/z 10 to m/z 500 for neat polymer samples and from m/z 10 to m/z 250 for polymer/catalyst samples. Mass spectral library searches employed a 38,000 spectra NBS library.

II.2 Thermogravimetry-Mass Spectrometry (TG-MS)

Thermogravimetric (TG) analysis was employed to study the effects of different catalysts on polymer decomposition processes. This method measures changes in sample mass as a function of temperature but gives no direct information regarding what species is lost from samples during heating. The combination of mass spectrometry with thermogravimetric analysis provides structural information regarding species evolved during sample weight losses detected by TG.

TG experiments were carried out by using a DuPont (Wilmington, DE) model 951 thermogravimetric analyzer. The 951 TG analyzer could heat samples from ambient temperature to 1200 °C. The original TG analyzer purge gas inlet was
modified to permit faster sample purging by directing the purge gas through the TG balance axially. A coarse glass frit was placed at the TG gas inlet to improve purge gas dispersion. A Hewlett-Packard (Palo Alto, CA) 5985 quadrupole mass spectrometer was connected to the TG analyzer gas outlet via a Swagelok 1/4 in. to 1/16 in. reducing union and a MCVT-1-50 variable split valve (Scientific Glass Engineering Inc., TX) (Figure II.4). The distance between the mass spectrometer ion source and TG analyzer furnace was about 12 inches. The split valve was used to shut off gas flow into the mass spectrometer when changing samples to avoid having to vent the mass spectrometer vacuum system each time a new sample was analyzed. It was also used to adjust the amount of TG effluent allowed to enter the mass spectrometer so that excessive ion source pressure could be avoided. The layout of the TG-MS system is shown in Figure II.5. To avoid condensation of evolved species in the TG-MS interface, the interface was enclosed in a heated aluminum box, shown as a dotted line in Figure II.5. The interior of the box was heated by four 1 in. x 6 in., 100 watt strip heaters. The heated air inside the box was circulated by using a model 8500C fan (Pamotor, CA). The interface temperature was monitored and controlled by an Omega CN 76000 programmable temperature controller (Omega engineering, CT). The interface temperature was maintained at 200 °C for studies described here.

All TG-MS experiments were performed with a 50 ml/min helium purge maintained by using a model 825 mass flow controller and model 1605 controller unit (Edwards High Vacuum Inc., NY). Sample heating rates of 1, 10, 25, and 50
Figure II.4 TG-MS interface.
Figure II.5 TG-MS apparatus.
°C/min were employed to determine kinetic parameters. The mass spectrometer ionization energy was 70 eV and the ion source temperature was maintained at 200 °C during all TG-MS experiments. TG and MS data acquisition were manually started at the same time so that mass spectral features and sample weight loss information could be correlated.

II.3 Thermogravimetry-Gas Chromatography/Mass Spectrometry (TG-GC/MS)

In some cases, mass spectra obtained during TG-MS analyses could not be used to profile the temperature dependent evolutions of the primary volatile products because species-specific ions could not be identified. To solve this problem, the TG-MS interface was modified by inserting a home-made capillary gas chromatograph between the thermogravimetric analyzer and mass spectrometer. In this manner, it was possible to separate the volatile products produced in the TG analyzer prior to mass analysis.

Figure II.6 shows a diagram of the TG-GC/MS interface. The interface consisted of two ovens. The top oven was a 30 cm x 25 cm x 15 cm insulated aluminum box that was heated by two 3 in. x 10 in. strip heaters. The temperature of the top oven was maintained at 200 °C and controlled by an Omega CN 76000 programmable temperature controller (Omega Engineering, CT). This oven contained a Valco eight port injection valve (Houston, TX) and two split valves.
Figure 11.6 TG-GC/MS interface.
When the injection valve was switched, the TG effluent trapped in the sample loop was directed into the capillary GC column. The two MCVT-1-50 split valves (Scientific Glass Engineering Inc., TX) were used to control TG-MS and TG-GC/MS gas flow into the mass spectrometer. For TG-MS experiments, the TG effluent went through the injection valve sample loop, bypassed the GC column, and passed through a split valve into the mass spectrometer. During TG-GC/MS experiments, the TG effluent went through the injection valve sample loop, passed through the capillary GC column and then entered the mass spectrometer. The bottom interface oven (20 cm x 16 cm x 15 cm) served as the capillary GC oven. It contained a 10 m x 0.25 mm DB-5 fused silica capillary column with a 0.32 \( \mu \)m stationary phase film thickness. The GC oven was heated by two 3 in. x 5 in. strip heaters. The capillary GC oven temperature was monitored and controlled by an Omega CN 2011 programmable temperature controller (Omega Engineering, CT).

II.4 Catalyst Surface Area Measurements

A FlowSorb II 2300 surface area analyzer (Micromeritics Instrument Corp., GA) was employed to measure catalyst surface areas. A schematic diagram of the FlowSorb II is shown in Figure II.7[2]. The surface areas of solid samples were measured by determining the quantity of gas that adsorbed as a monolayer on sample surfaces. Monolayer adsorption of nitrogen was established at atmospheric pressure and liquid nitrogen temperature by using a 30% nitrogen - 70% helium (by
Figure II.7 Diagram of the FlowSorb II 2300 surface area analyzer.
volume) mixture. All measurements were carried out by using the single-point method\cite{2} with the 30\% N\textsubscript{2}/70\% He mixture flowing at 60 ml/min.

Before making surface area measurements, catalyst samples were left in an oven at 150 °C for 24 hours and then degassed by heating them to 250 °C for at least one hour with a heating mantle. Prior to sample measurements, the FlowSorb II was calibrated by the method suggested by the manufacturer\cite{2}. The calibration was performed by using a gas-tight syringe to inject 1 ml of pure N\textsubscript{2} into the instrument through the septum. The reading on the display meter should be 2.84 ± 0.02. A cold trap cooled by a dewar filled with liquid nitrogen was used to remove volatile impurities such as water vapor from the gas mixture. Samples were placed in U-tubes for degassing and analysis. The adsorption measurement was initiated by cooling the sample in the U-tube with a dewar filled with liquid nitrogen. After adsorption was completed, the total sample surface area was calculated from measured pressure changes by using the Brunauer-Emmet-Teller (BET) method and recorded by the device. A desorption measurement was started by removing the dewar of liquid nitrogen from the sample tube and bringing the sample to room temperature. For all catalyst samples, adsorption and desorption measurements resulted in comparable results. Surface areas reported here were the average of these two measurements.
II.5 Poly(ethylene) Molecular Weight Measurement

It has been found that the molecular weights of polymers have significant influences on their chemical and physical properties\cite{3}. Measurements of polymer molecular weights are therefore a matter of fundamental importance for the characterization of polymeric materials. Two poly(ethylene) and two poly(styrene) samples were used in this study. The two poly(styrene) samples were purchased from Aldrich Chemical Co. These two poly(styrene) samples were standard references for gel permeation chromatography and their molecular weights were well known and reported by the manufacturer to be 2,700 amu and 850,000 amu. The molecular weight of the poly(ethylene) sample obtained from Polysciences Inc. was reported by the manufacturer to be 700 amu. However, Aldrich provided no information regarding the molecular weight of their poly(ethylene).

The intrinsic viscosity method was used to measure viscosity average molecular weights\cite{4,5} for the poly(ethylene) sample obtained from Aldrich. This is a simple technique widely used for molecular weight determination, and is based on the determination of the intrinsic viscosity, \([\eta]\), of a polymer in solution by measurements of solution viscosity\cite{6-8}. This method requires measurement of the time (t) that it takes a specified volume of polymer solution to flow through a length of capillary tubing. This time is proportional to the viscosity (\(\eta_s\)) of the solution, which is a function of the polymer molecular weight. The flow time and viscosity for the pure solvent (\(t_o\) and \(\eta_o\)) are also needed to determine the polymer
molecular weight. The relative viscosity (\( \eta_r \)) is defined as the ratio of the viscosity of the polymer solution to that of the solvent and is approximately equal to the ratio of the solution and solvent flow times if the densities of the two are comparable.

\[
\eta_r = \frac{\eta}{\eta_o} = \frac{\rho f}{\rho_o f_o} = \frac{t}{t_o}
\]

(2.1)

The specific viscosity \( \eta_{sp} \) is obtained from the relative viscosity by subtracting one unit from \( \eta_r \):

\[
\eta_{sp} = \eta_r - 1 = \frac{t}{t_o} - 1
\]

(2.2)

The specific viscosity is a measure of the increase in viscosity that results from the addition of polymer to the solvent. The specific viscosity is zero at infinite dilution.

The intrinsic viscosity \([\eta]\) is derived from the specific viscosity by:

\[
[\eta] = \lim_{c\to\infty} \frac{\eta_{sp}}{c}
\]

(2.3)

where \( c \) is the number of grams of polymer contained in 100 ml of solution.

Huggins proposed a relationship between the quantity, \( \eta_{sp}/c \), and the concentration of dilute polymer solutions:

\[
[\eta] = K [\eta]^n
\]

(2.4)

where \( K \) and \( n \) are constants depending on the polymer and solvent system.


\[ \frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2c \quad (2.4) \]

where \( k' \) is the dimensionless Huggins viscosity constant and depends on the solvent, temperature and polymer structure. This constant characterizes polymer-polymer interactions in the solvent and has values in the range of 0.2 to above 0.5\(^{[8,9]} \).

From the above equation, a plot of \( \eta_{sp}/c \) versus \( c \) will be linear with \( [\eta] \) as the intercept. The relationship between polymer molecular weight and \( [\eta] \) is expressed by the well known Mark-Houwink equation\(^{[6,8]} \):

\[ [\eta] = KM_v^\alpha \quad (2.5) \]

where \( \alpha \) and \( K \) are empirical constants that are specific for a given polymer, solvent and measurement temperature and \( M_v \) is the polymer viscosity average molecular weight.

Four poly(ethylene) solutions with concentrations of 0.2007, 0.4009, 0.6004, and 0.8001 g/dl were prepared by dissolving appropriate amounts of poly(ethylene) in decaline (Eastman Kodak Co., NY) at 135 °C. Solution temperatures were maintained by using an oil bath. Before measurements, the solutions and a clean Ostwald type viscometer were immersed in the oil bath for at least 10 minutes to allow equilibration at the bath temperature (135 °C). The viscometer was mounted vertically and was used to measure the viscosities of all four solutions. Five ml
 aliquots of polymer solutions or decaline were transferred into the viscometer for measurements. The flow times required for the solutions to travel between the upper and lower marks on the viscometer were measured with a stopwatch. For each solution, three separate measurements were taken and the values reported here are the averages of these measurements. Specific viscosity values were calculated from the flow times and are listed in Table II.1.

<table>
<thead>
<tr>
<th>c (g/dl)</th>
<th>$\eta_{sp}$</th>
<th>$\eta_{sp}/c$ (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2007</td>
<td>0.35 ± 4 x $10^{-5}$</td>
<td>1.73 ± 2 x $10^{-4}$</td>
</tr>
<tr>
<td>0.4009</td>
<td>0.73 ± 2 x $10^{-3}$</td>
<td>1.82 ± 4 x $10^{-3}$</td>
</tr>
<tr>
<td>0.6004</td>
<td>1.12 ± 3 x $10^{-3}$</td>
<td>1.87 ± 5 x $10^{-3}$</td>
</tr>
<tr>
<td>0.8001</td>
<td>1.55 ± 4 x $10^{-3}$</td>
<td>1.94 ± 5 x $10^{-3}$</td>
</tr>
</tbody>
</table>

By plotting $\eta_{sp}/c$ versus c (Figure II.8), $[\eta]$ was obtained from the intercept, which was 1.68 ± 1 x $10^{-2}$ dl/g. By using K and $\alpha$ values for poly(ethylene) in decaline at 135 °C from the literature\textsuperscript{14,51}, the Mark-Houwink equation becomes:

$$[\eta]_{\text{decaline,135°C}} = 6.2 \times 10^{-4} M^{0.7}$$  \hspace{1cm} (2.6)

The calculated molecular weight for the poly(ethylene) was $8.03 \times 10^{4} \pm 7 \times 10^{2}$.
Figure II.8 Plot of $\eta_{sp}/C$ versus $C$ for the HPE sample.
II.6 $^{13}$C-NMR Measurements

Solid-state $^{13}$C-NMR spectra were measured on a Varian Unity Plus 400 spectrometer. A poly(ethylene) powder sample (ca. 0.5 g) was packed into a 7 mm o.d. Si$_3$N$_4$ rotor for solid-state $^{13}$C-NMR measurements. The spinning rate of the sample rotor was set to 6 kHz. The cross-polarization magic-angle spinning (CP-MAS) technique and a magic-angle supersonic-spinning solid NMR probe (Doty Scientific, Inc., SC) were used to obtain high resolution NMR spectra. A Varian XL-300 spectrometer was used for liquid phase $^{13}$C-NMR measurements. About 0.1 g of poly(ethylene) was dissolved in 0.5 ml of 1,2,4-trichlorobenzene at 130 °C to prepare samples for liquid phase $^{13}$C-NMR analysis. To these mixtures, 0.05 ml of CDCl$_3$ and 0.05 ml of hexamethyldisiloxane were added at 130 °C. About 0.1 g of poly(styrene) samples were dissolved in 0.5 ml of 1,2,4-trichlorobenzene at 90 °C. To these mixtures, 0.05 ml of CDCl$_3$ and 0.05 ml of hexamethyldisiloxane were added at 90 °C. Poly(ethylene) and poly(styrene) polymers were completely dissolved in solvent and the mixtures appeared to be homogeneous at 130 and 90 °C, respectively. Sufficient CDCl$_3$ was present to maintain a lock signal for poly(ethylene) and poly(styrene) liquid phase $^{13}$C-NMR measurements. Hexamethyldisiloxane was used as an internal reference.
II.7 Data Acquisition and Handling

Data acquisition and handling are described in this section. Methods for the calculation of overall volatilization activation energies and activation energies for the production of specific products or product classes are also described in this section.

II.7.1 Mass Spectral Data Acquisition

Pyrolysis GC/MS, TG-MS and TG-GC/MS mass spectra were acquired by using a Teknivent (St. Louis, MO) Vector/One™ data acquisition module driven by an IBM compatible personal computer. The data acquisition software automatically stored elapsed times and scan numbers with mass spectral data files. Mass spectral data files were converted to ASCII files by a program called "MS-AXUM" written by Dr. Robert White, so that this data could be plotted by using "AXUM" plotting software. For pyrolysis GC/MS experiments, the scan numbers recorded were used to calculate the times at which mass spectra were acquired:

\[
\text{time} = \frac{\text{scan} \times (\text{scan rate})}{60} \quad (\text{min}) \tag{2.7}
\]

where scan represents scan number, and scan rate is the MS data acquisition rate (seconds/scan). For TG-MS and TG-GC/MS experiments, the scan numbers were
used to calculate the sample temperatures at which mass spectra were acquired:

\[
\text{temperature} = \frac{\text{scan} \times (\text{scan rate})}{60} \times (\text{heating rate}) + T_0 \ (°C) \quad (2.8)
\]

where heating rate is the TG sample heating rate (°C/min) and \( T_0 \) is the initial temperature at which the TG experiment was started.

II.7.2 Thermogravimetric Data Acquisition

Thermogravimetric data acquisition was performed by using a DuPont (Wilmington, DE) Thermal Analyst 2000 system. This data acquisition system could control the sample temperature, track the progress of experiments in real time, and store sample mass and temperature data. After TG experiments, elapsed times, temperatures, and sample mass information were saved in a TG data file for later processing. The data files could be converted into ASCII format, so that this information could be plotted by using the "AXUM" program.

II.7.3 GC/MS Chromatogram Curve Fitting

A curve fitting algorithm developed in the laboratory was used to deconvolute gas chromatographic overlapping peaks and to calculate peak areas. This program used the exponentially modified Gaussian function to model
chromatographic peak shapes, which were defined by retention time, peak height, peak standard deviation and an exponential damping factor. After starting the program, convergence criteria, maximum run time, allowed peak center shifts, average peak widths, and a peak picking threshold level were specified. During the curve fitting process, the program could be stopped and resumed at any time in order to manually adjust peak positions and shapes by using function keys. Curve fitting results were stored in a data file and consisted of retention time, peak intensity, area, and exponential damping factor for each GC-MS peak. The curve fitting peak areas generated from total ion current chromatograms were used to semiquantitatively determine pyrolysis product distributions. Figure II.9 shows the results of applying curve fitting to a chromatogram. This chromatogram was obtained from 600 °C pyrolysis of a sample comprised of low molecular weight poly(ethylene) coated on HZSM-5 catalyst and contains 85 peaks. The solid line in Figure II.9 represents the measured chromatogram. The dotted line in Figure II.9 represents the curve fitting result. Figure II.10 shows an expanded view of a selected region of Figure II.9. The measured and fitted peaks are clearly in good agreement, therefore the peak areas derived from curve fitting should be of reasonable accuracy for semiquantitative comparison.

Volatile product distributions derived from chromatograms were expressed as percentages of integrated total ion current. The uncertainty of the results was estimated by comparing peak areas obtained from two chromatograms measured under the same conditions. This yielded an error estimate of ±2%.
Figure II.9 Curvefitting result for pyrolysis GC/MS chromatogram of LPE/HZSM-5 sample obtained at 600 °C.
Figure II.10 Expanded view of the curvefitting result shown in Figure II.9.
II.7.4 Calculation of TG Volatilization Kinetic Parameters

Thermogravimetric analysis has been used extensively to evaluate the kinetics of polymer degradation processes\textsuperscript{10-13}. All of the many methods used to calculate kinetic parameters are derived from the Arrhenius equation:

\[
\frac{-dc}{dt} = A \cdot \frac{E_a}{R \cdot T} \cdot c^n
\]  

(2.9)

where \(-dc/dt\) is the decomposition reaction rate, \(A\) is the reaction frequency factor, \(E_a\) is the activation energy, \(n\) is reaction order, and \(c\) is reactant concentration. In the Freidman method\textsuperscript{13}, kinetic parameters are derived from several TG curves measured by using different linear heating rates. Modifying the Arrhenius equation for the derivation of Friedman's method gives:

\[
-
\frac{1}{w_o - w_f} \frac{dw}{dt} = A \cdot \frac{E_a}{R \cdot T} \cdot f\left(\frac{W}{W_o}\right)
\]  

(2.10)

where \(dw/dt\) is the rate of change of the sample weight calculated at a sample fractional weight of \(W\), \(w_o\) is the initial sample weight, \(w_f\) is the residual weight of the sample after all volatiles have been evolved, \(E_a\) is the sample volatilization activation energy, \(A\) is the frequency factor for the overall volatilization process, \(R\) is the gas constant (1.987 cal/K·mol), and \(T\) is the absolute sample temperature.
The fractional sample weight $W_r$ is a function of the sample weight $w$ measured by TG:

$$W_r = \frac{w - w_f}{w_o - w_f} \quad (2.11)$$

Applying the natural logarithm to both sides of the Freidman equation gives:

$$\ln \left[ -\frac{1}{w_o - w_f} \frac{dw}{dt} \right] = \ln(A) + \ln[f(W_r)] - \frac{E_a}{RT} \quad (2.12)$$

where $f(W_r)$ is some function of the sample weight. Freidman assumed that the reaction order was independent of temperature and dependent only on the instantaneous fractional weight of the sample. Values of $(dw/dt)$ and $(1/T)$ at selected $W_r$ values can be obtained from multiple TG measurements in which the heating rate is varied. A plot of $\ln[(-1/(w_o-w_f)(dw/dt))]$ versus $(1/T)$ exhibits a straight line. The activation energy is obtained from the slope $(-E_a/R)$ by multiplying it by $-R$. $A$ and $n$ information is contained in the intercept $(\ln(A) + \ln[f(W_r)])$.

Freidman proposed that the weight function $f(W_r)$ could be written in the form of:

$$f(W_r) = (W_r)^n \quad (2.13)$$
where $n$ is the reaction order. Multiplying both sides of the above equation by $A$ and then taking the natural logarithm of both sides yields:

$$\ln[A \cdot f(W_\text{p})] = \ln(A) + n \ln(W_\text{p})$$  \hspace{1cm} (2.14)

If the proposed form of the weight function $f(W_\text{p})$ is correct, a straight line can be obtained by plotting $\ln[A f(W_\text{p})]$ versus $\ln(W_\text{p})$, for which the slope is $n$ and the intercept is $\ln(A)$. Thus, it is possible to obtain all three kinetic parameters by using the Freidman technique. One advantage of the Freidman technique over other methods is that no assumption is made for the value of one kinetic parameter to obtain values for the other two kinetic parameters. Another advantage of the Freidman technique is that kinetic parameters are calculated from multiple TG experiments. Most other methods use only one TG curve to calculate reaction order and activation energy and therefore can provide no error estimates. Error estimates of activation energies were calculated from the standard deviations of the slopes of plots of $\ln[-1/(w_o \cdot w_p)(dw/dt)]$ versus $(1/T)$. The calculation method is described below\textsuperscript{[14]}.

Assume that the equation for a straight line is:

$$y = mx + b$$  \hspace{1cm} (2.15)

where $m$ is the slope and $b$ is the intercept on the $y$-axis. By using the method of least squares, the following equations can be obtained, which will be used for
further calculation.

\[ C = \Sigma x^2 - \frac{(\Sigma x)^2}{n} \quad (2.16) \]

\[ D = \Sigma y^2 - \frac{(\Sigma y)^2}{n} \quad (2.17) \]

In the above equations, \( n \) is the number of data points. The slope and intercept of the best fit line can be calculated as follows:

\[ m = \frac{\Sigma xy - (\Sigma x \Sigma y)}{n \cdot C} \quad (2.18) \]

\[ b = \frac{\Sigma y - m\Sigma x}{n} \quad (2.19) \]

The standard deviation of the y-values, \( s_y \), is given by:

\[ s_y = \sqrt{\frac{(D - m^2 C)}{n - 2}} \quad (2.20) \]

and the standard deviation of the slope, \( s_m \), can be obtained from:

\[ s_m = \frac{s_y}{\sqrt{C}} \quad (2.21) \]
Activation energy error estimates reported here are the slope standard deviations derived from linear regression analysis of the plots used to obtain activation energies.

II.7.5 Determination of Activation Energies for Evolution of Specific Products by TG-MS

As mentioned before, information regarding specific volatile products or structural classes of products can be obtained by interfacing a mass spectrometer to a TG analyzer. By plotting the intensity of selected ions as a function of TG temperature, species-specific temperature profiles can be constructed. For polymer thermal decompositions, we have found that these temperature profiles can be quite different because the activation energies for forming different species may differ\textsuperscript{[15-17]}. Therefore, in addition to the overall volatilization activation energy derived from weight loss measurements, activation energies for the production of specific products or product classes were also calculated. This was accomplished by employing the technique of linear programmed thermal degradation mass spectrometry described by Risby and Yergey\textsuperscript{[18,19]}. This method is based on the consideration that when sample temperature is increased linearly, a sample can be thermally decomposed into various species. These species may have different evolution profiles and exhibit different evolution rate maxima depending upon the heating rate, activation energies and frequency factors for the formation of each
species. If a species-specific ion can be found, the concentration of a given species can be measured mass spectrometrically and the rate of the reaction that produces a given species can be related to the mass spectrometer ion current for the species-specific ion.

The relationship between relevant parameters derived from the Arrhenius equation by Risby and Yergey\cite{18,19} is:

\[
\ln \frac{M}{T_{m_j}^2} + \ln \frac{E_j}{R K_{m_j}} = -\frac{E_j}{R} \left( \frac{1}{T_{m_j}} \right) \quad (2.22)
\]

where \(T_{m_j}\) is the temperature that corresponds to the maximum rate for evolution of species \(j\), \(E_j\) is the activation energy for the formation of species \(j\), \(K_{m_j}\) is the frequency factor of the reaction, \(M\) is the heating rate, and \(R\) is the gas constant. This expression is independent of the order of the reaction. If a series of temperature ramps are used for TG-MS measurements, values for \(E_j\) and \(K_{m_j}\) can be obtained from the slope and intercept of a plot of \(\ln[M/T_{m_j}^2]\) versus \(1/T_{m_j}\).

II.8 Reagents and Sample Preparation Methods

The HZSM-5 zeolite was obtained from Mobil Oil (Paulsboro, NJ) and was characterized by a 1.5% alumina content and pore size of 5.5 x 5.7 Å. The silica-alumina catalyst was obtained from Condea Chemie GmbH (Hamburg, Germany). The silica-alumina (Si-Al) catalyst contained 11.8% alumina by weight. The
sulfated zirconia (ZrO_2/SO_4) catalyst was synthesized by following procedures described in the literature^{[20]}. Zirconium hydroxide precursor was precipitated from a 0.5 M zirconium tetrachloride solution by dropwise addition of NH_4OH. Sulfate addition was accomplished by incipient wetness impregnation with an NH_4SO_4 solution. After drying, the catalyst was calcined in air at 600 °C for 4 hours. The ZrO_2/SO_4 catalyst contained 6% by weight sulfate. All catalysts were used without additional purification. One poly(ethylene) sample was purchased from Aldrich Chemical Company (Milwaukee, WI). The molecular weight of this polymer was 80,000 amu as reported in Section II.5. The other poly(ethylene) sample (MW = 700) was purchased from Polysciences Inc. (Warrington, PA). Standard high (MW = 850,000 amu) and low (MW = 2,700 amu) molecular weight poly(styrene) samples were purchased from Aldrich Chemical Company. All poly(ethylene) and poly(styrene) samples were used directly without additional purification. n-Decane (99%) (Sigma Chemical Co., MO) and cyclohexane (99%) (Aldrich, WI) were used as solvents to dissolve poly(ethylene) and poly(styrene), respectively. Helium (99.9995%), and the 30% N_2/70% He mixture were purchased from Union Carbide Corp., Linde Division (Danbury, CT). To make approximately 10% w/w poly(ethylene)/catalyst samples, an appropriate amount of polymer was added into 10 ml of decane (b.p. 174 °C), and the mixture was heated until the poly(ethylene) was completely dissolved. After a homogeneous solution was obtained, an appropriate amount of catalyst was added to the poly(ethylene) solution. Then, the mixture was rotoevaporated for three to four hours to ensure the complete removal
of solvent. The resulting poly(ethylene) coated catalyst samples were dried for several hours at 120 °C. This procedure was repeated to prepare 10% w/w poly(styrene) coated catalyst samples. However, cyclohexane (b.p. 80.7 °C) was used as the solvent to dissolve poly(styrene) and the resulting poly(styrene) coated catalyst samples were dried for several hours at 90 °C. The 10% w/w polymer/catalyst samples were analyzed by pyrolysis-GC/MS, TG-MS and TG-GC/MS.

II.9 Characterization of Catalysts

Surface areas of the catalysts used in this study were measured by the method described in Section II.4. Results from surface area measurements of the three catalysts are given in Table II.2.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica-Alumina</td>
<td>211 ± 10</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>354 ± 8</td>
</tr>
<tr>
<td>ZrO₂/SO₄</td>
<td>157 ± 7</td>
</tr>
</tbody>
</table>

TG-MS experiments were carried out to study the thermal properties of the
neat catalysts. All three catalysts were heated in He from 50 to 1000 °C at 10 °C/min. The TG weight loss curves for the three catalysts are shown in Figure II.11. Weight loss began to occur below 100 °C for all three catalysts. The HZSM-5 catalyst showed a rapid weight loss at temperatures below 250 °C but little above 250 °C. The weight loss curve for the Si-Al catalyst consisted of two segments with different slopes. The weight loss rate for this catalyst was greater at temperatures below 250 °C. Mass spectral information obtained during TG-MS analyses revealed that Si-Al and HZSM-5 catalyst weight losses could be attributed to the evolution of water. The ZrO$_2$/SO$_4$ catalyst exhibited two weight loss steps. The first step corresponded to the evolution of water and the second step, starting at about 625 °C, corresponded to SO$_2$ evolution that resulted from the decomposition of the catalyst.

The acidic properties of catalysts used in this study were investigated by temperature-programmed desorption (TPD) of ammonia. TG-MS was employed for TPD experiments so that volatile products evolved when catalyst samples were heated could be identified. Prior to addition of NH$_3$ adsorbate, samples were heated to 600 °C in the TG sample chamber and allowed to cool under vacuum so that H$_2$O absorbed on the catalyst surface was removed. After samples had cooled down to 100 °C, NH$_3$ was added to the TG sample chamber to attain a pressure of 10 torr. After equilibration for about 5 to 10 minutes, He was then added to the sample chamber until the total pressure exceeded atmospheric pressure. At this point, a valve was opened to allow He flowing into the sample chamber to exit.
Figure II.11 TG weight loss curves for neat Si-Al, HZSM-5, and ZrO₂/SO₄ catalysts.
Figure II.12 TG and DTG curves obtained from NH$_3$-TPD experiment for HZSM-5 catalyst.
Figure II.12 shows the TG curve and its derivative (DTG) curve for NH$_3$ desorption from the HZSM-5 catalyst obtained by heating the sample at a rate of 10 °C/min from 100 to 800 °C. The TG and DTG curves exhibit two weight loss steps. This indicates that there are two different types of acid sites on the HZSM-5 surface. TG-MS mass spectral information confirmed that these two weight loss steps corresponded to NH$_3$ desorption. The mass spectral ion signal temperature profile (Figure II.13) for desorbed NH$_3$ (m/z 17) is in good agreement with the DTG curve in Figure II.12. The TG and MS results shown in Figures II.12 and II.13 are consistent with previous HZSM-5 zeolite NH$_3$-TPD results$^{[21]}$. Figure II.14 shows the TG and DTG curves for NH$_3$ desorption from the ZrO$_2$/SO$_4$ catalyst. The TG curve consists of four weight loss steps, and the corresponding DTG curve exhibits four peaks. Mass spectral information indicated that volatile products generated above 400 °C during TG-MS analysis were CO$_2$ and SO$_2$ which resulted from the thermal decomposition of the catalyst. The ion signal temperature profile for NH$_3$ (m/z 17) contains two broad unresolved peaks (Figure II.15), indicating the overlap of NH$_3$ desorbing from different sites over a relatively broad temperature range. This behavior is consistent with results reported in literature$^{[22]}$. The Si-Al TG curve for NH$_3$-TPD (Figure II.16) reveals two weight loss steps. Mass spectral information obtained during TG-MS analysis indicated that the first weight loss step corresponded to NH$_3$ desorption and the second weight loss step was due to the evolution of H$_2$O. Figure II.17 shows the NH$_3$ ion signal temperature profile obtained for the Si-Al sample. It is very noisy but clearly contains two broad
Figure II.13 NH₃ temperature profile derived from HZSM-5 TPD TG-MS analysis.
Figure II.14 TG and DTG curves obtained from NH₃-TPD experiment for ZrO₂/SO₄ catalyst.
Figure II.15 NH₃ temperature profile derived from ZrO₂/SO₄ TPD TG-MS analysis.
Figure II.16 TG and DTG curves obtained from NH₃-TPD experiment for Si-Al catalyst.
Figure II.17 NH$_3$ temperature profile derived from Si-Al TPD TG-MS analysis.
unresolved peaks at temperatures below 350 °C, suggesting that there were at least two different acid sites on this catalyst. The mass of NH₃ desorbed during weight loss steps was used to determine the number of acid sites on catalyst surfaces. Acid site densities for the three catalysts are compiled in Table II.3.

Table II.3 Catalyst Acid Site Densities

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Acid Site Density (sites/nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>Low temperature sites: 1.0</td>
</tr>
<tr>
<td></td>
<td>High temperature sites: 1.1</td>
</tr>
<tr>
<td>ZrO₂/SO₄</td>
<td>5.1</td>
</tr>
<tr>
<td>Si-Al</td>
<td>1.3</td>
</tr>
</tbody>
</table>

*a*Low temperature sites correspond to the NH₃ evolution below 300 °C; High temperature sites correspond to the NH₃ evolution above 300 °C.
References


Chapter III
Catalytic Cracking of Poly(ethylene)

III.1 Background

Poly(ethylene) (PE) was first synthesized by polymerizing ethylene monomer in the laboratories of Imperial Chemical Industries, England, in 1933\textsuperscript{[1-3]}. The polymerization reaction was initiated by trace amounts of oxygen and conducted either in high-pressure autoclaves or in continuous tubular reactors operating at temperatures near 250 °C and pressures as high as 3000 atm\textsuperscript{[1]}. However, because the polymerization reaction was excessively exothermic (the heat of ethylene polymerization is 105 kcal/mol\textsuperscript{[11]} and required strict control of reaction conditions and elaborate safety measures, poly(ethylene) was not commercially available until 1939\textsuperscript{[2]}. Today, poly(ethylene) accounts for 31% of plastics produced worldwide\textsuperscript{[4]}. There are two polymerization techniques used commercially today to produce PE. One is free radical initiated polymerization at high pressure and elevated temperature. The second technique is transition metal catalyzed polymerization conducted at or near atmospheric pressure and room temperature\textsuperscript{[5]}. Commercial poly(ethylene) has been classified into three categories according to density:
Poty(ethylene) Class | Density Range (g/cm³) | Acronym
---|---|---
Low density | 0.910 - 0.925 | LDPE
Medium density | 0.926 - 0.940 | MDPE
High density | ≥ 0.941 | HDPE

Poly(ethylene) is essentially a long chain of methylene groups with some short-chain branches. The amount of short-chain branching determines the degree of crystallinity and therefore PE density\(^{[31]}\). In PE made by the low pressure process, few branches are found. In PE made by the high pressure process, significantly more branches are present\(^{[6]}\). Thus, differences in the physical properties of high and low density PE can be attributed to the type and frequency of short-chain branches along the polymer backbone. LDPE uses include packaging, such as sandwich, trash and refuse bags, industrial liners, etc. HDPE is primarily used to manufacture blow molded containers and related products including bottles for household and automotive chemicals, milk and other foods. PE made by the high pressure process is primarily LDPE, but some MDPE can also be made by this process. High density poly(ethylene) (HDPE) is produced by the low pressure process.

The thermal decomposition of PE has been the subject of numerous studies\(^{[7-14]}\). A radical mechanism for the thermal degradation of poly(ethylene) was proposed by Wall and Sidney\(^{[8]}\). Chain end radicals are formed in the initial decomposition step by the random scission of C-C bonds in the polymer chain:
Primary radicals can undergo depropagation, or intra- or intermolecular hydrogen transfer reactions. Depropagation via β-scission yields shorter chain end radicals and ethylene monomer:

\[
\text{R} - \text{CH}_2 - \left(\text{CH}_2\right)_{n-2} \cdot \text{CH}_2 \longrightarrow \text{R} - \text{CH}_2 - \left(\text{CH}_2\right)_{n-2} \cdot \text{CH}_2 + \text{CH}_2=\text{CH}_2
\]  

Intermolecular hydrogen transfer occurs by abstraction of a hydrogen atom from a neighboring poly(ethylene) molecule leading to the formation of a more stable secondary radical:

\[
\begin{align*}
\text{R} - \text{CH}_2 - \left(\text{CH}_2\right)_{n-1} \cdot \text{CH}_2 + \text{CH}_2=\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{R}' & \longrightarrow \text{R} - \text{CH}_2 - \left(\text{CH}_2\right)_{n-1} \cdot \text{CH}_2 + \text{CH}_2=\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{R}' \\
& \text{(A)} \quad \text{(B)} \quad \text{(C)} \quad \text{(D)} \\
\end{align*}
\]

Secondary radicals can decompose to form n-alkanes, n-alkenes or alkadienes.

\[
\text{R} - \text{CH}_2 - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{R}' \\ \\
\text{(E)} \quad \text{(F)} \quad \text{(G)}
\]

Radical (F) can abstract a hydrogen atom from another molecule and form CH\textsubscript{3}R'.
which may be either an alkane or alkene, depending on whether R' is saturated or unsaturated. The unsaturated product, (G), can be either an alkene or an alkadiene.

Intramolecular hydrogen transfer (back-biting) via pseudocyclization by abstracting a hydrogen atom located at the fifth position relative to the carbon atom with the unshared electron results in the formation of a more stable secondary radical.

\[
R - \text{CH}_2 - \text{CH} - \text{CH} - \text{CH} - \text{CH} - \text{CH} - \text{CH}_3 \quad (6)
\]

Radicals formed by back-biting may undergo further back-biting reactions:

\[
R - \text{CH}_2 - \text{CH} - \text{CH} - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \quad (7)
\]

or may undergo $\beta$-scission:

\[
R - \text{CH}_2 - \text{CH} - \text{CH} - \text{CH}_2 - (\text{CH}_2)_n - \text{CH}_3 \quad (H)
\]

\[
R^* + \text{CH}_2 = \text{CH}_2 - (\text{CH}_2)_n - \text{CH}_3 \quad (I)
\]

\[
R - \text{CH}_2 - \text{CH} = \text{CH}_2 + \text{CH}_2 - (\text{CH}_2)_{n-2} - \text{CH}_3 \quad (J)
\]
Depending on whether R is saturated or unsaturated, product (K) may be an alkene or an alkadiene. The primary radical (J) produced in reaction (9) can abstract a hydrogen atom from another molecule to form an alkane:

\[
\text{CH}_2-(\text{CH}_2)_n-\text{CH}_3 \xrightarrow{\text{H}^-} \text{CH}_3-(\text{CH}_2)_{n+2}-\text{CH}_3
\]  

(10) 

Intermolecular hydrogen transfers followed by β-scission (e.g. reactions (3), (4), and (5)) are considered to be the most important degradation pathways for poly(ethylene)\textsuperscript{11,12}. These reactions result in a large decrease in average molecular weight before any volatile products are produced\textsuperscript{12}. Intramolecular hydrogen transfers followed by β-scission (e.g. reactions (6) - (9)) occur near 400 °C\textsuperscript{11,12,16} but have less of an effect on molecular weight than lower temperature pathways.

Radicals may be consumed by disproportionation or recombination reactions\textsuperscript{11,12,15}:

\[
\text{R-CH}_2 + \text{CH}_2-\text{R}' \rightarrow \text{R-CH}_2-\text{CH}_2-\text{R}'
\]  

(11) 

\[
\text{R-CH}_2 + \text{R}'-\text{CH}-\text{R}'' \rightarrow \text{R-CH}_2-\text{CH}-\text{R}'
\]  

(12) 

\[
\text{R-CH}_2-\text{CH}_2 + \text{CH}_2-\text{R}' \rightarrow \text{R-CH}=\text{CH}_2 + \text{CH}_3-\text{R}'
\]  

(13) 

\[
\text{R-CH}_2 + \text{R}'-\text{CH}-\text{CH}_2-\text{R}'' \rightarrow \text{R-CH}_3 + \text{R}'-\text{CH}=\text{CH-}\text{R}''
\]  

(14)
The tendency for disproportionation increases with increasing temperature\textsuperscript{[17,18]}. It has been estimated that recombination of primary radicals is about ten times more likely than disproportionation at temperatures between 300 and 400 °C\textsuperscript{[19]}. However, for reactions between primary and secondary radicals, disproportionation is more favored than recombination\textsuperscript{[18]}.

Volatile PE decomposition products ranging from C\textsubscript{1} to C\textsubscript{90} have been detected by gas chromatography\textsuperscript{[20]}. Gas chromatograms of poly(ethylene) pyrolysates typically exhibit three sets of homologues\textsuperscript{[9,10,21,22]}. Triplet gas chromatographic elutions consist of an n-alkane, a 1-alkene and a terminal n-alkadiene, all having the same number of carbon atoms. The relative yields of the saturated and unsaturated products at each carbon number depend on decomposition temperature. Wampler et al\textsuperscript{[22]} found that the n-alkane yield decreased and the alkadiene yield increased when decomposition temperatures were increased.

The effect of chain branching on poly(ethylene) decomposition has also been studied\textsuperscript{[7,8,13,14,23]}. Chain branching lowers the thermal stability of the polymer and the presence of tertiary carbon atoms promote cleavage of the polymer backbone at carbon atoms α and β to the branch site. Alpha and β cleavages were found to occur with equal frequency\textsuperscript{[7,8,13,14,24]}. Like linear poly(ethylene), the decomposition of branched poly(ethylene) occurs by radical initiation, depropagation, hydrogen transfer and termination reactions. However, for branched poly(ethylene), intermolecular hydrogen transfer results in preferential abstraction of tertiary
hydrogen atoms:

\[ \text{H} - \text{CH}_2 + \text{CH}_2 - \text{CH}_2 \rightarrow \text{CH}_3 + \text{CH}_2 - \text{H} \]  \hspace{1cm} (15)

The tertiary radical may decompose to form an \( \alpha' \)-olefin and a primary radical:

\[ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \rightarrow \text{CH}_2 - \text{CH}_2 + \text{CH}_2 \]  \hspace{1cm} (16)

The \( \alpha \)-methylenic hydrogen in the \( \alpha' \)-olefin is even more easily abstracted than a tertiary hydrogen. Therefore, after a second intermolecular hydrogen abstraction, an allyl radical may be produced:

\[ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \rightarrow \text{CH}_2 - \text{CH}_2 + \text{CH}_2 \]  \hspace{1cm} (17)

The allyl radical may undergo \( \beta \)-scission to yield a substituted alkadiene:

\[ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \rightarrow \text{CH}_2 - \text{CH}_2 + \text{CH}_2 \]  \hspace{1cm} (18)

It is known that C-C bonds located in \( \beta \)-positions relative to double bonds are weaker than saturated C-C bonds. Thus, an \( \alpha' \)-olefin readily undergoes scission to produce an allyl radical:

\[ \text{CH}_2 - \text{CH}_2 - \text{C} = \text{CH}_2 \rightarrow \text{CH}_2 + \text{CH}_2 - \text{C} = \text{CH}_2 \]  \hspace{1cm} (19)
Intramolecular hydrogen transfer reactions of branched PE can form secondary radicals, which may further undergo β-scission to yield substituted volatile products.

\[
\begin{align*}
\text{H} & \quad \overset{\sim}{\text{C}}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH} \\
& \quad \rightarrow \overset{\sim}{\text{C}}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH} \\
\end{align*}
\]

\[
\begin{align*}
\text{R} & \quad \overset{\sim}{\text{C}}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH} \\
& \quad \rightarrow \overset{\sim}{\text{C}}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH} \\
\end{align*}
\]

Thermogravimetry provides a means to study the overall volatilization of PE. Volatilization activation energies for poly(ethylene) thermal degradation have been reported\(^{[7,25-30]}\). Several methods were used to obtain volatilization activation energies. With isothermal thermogravimetry, sample mass is recorded as a function of time at constant temperature. The rate of sample mass loss can be used to calculate volatilization activation energies. Alternatively, dynamic thermogravimetry can be employed. In this method, the sample is heated at a constant rate while mass loss is measured. Activation energies for sample volatilization can be determined from a single weight loss curve or from many curves obtained by varying sample heating rates. Another method for calculation of volatilization activation energies is by using factor-jump thermogravimetry, in which the magnitude of a rate-determining variable such as temperature, pressure, gaseous
flow rate, etc. is jumped in discrete steps. PE volatilization activation energies obtained by these methods are listed in Table III.1. The PE sample properties (such as molecular weight and branching), the method used to study samples, and the calculation method all influence the values obtained for the kinetic parameters. For example, Jellinek\textsuperscript{[7]} and Mucha\textsuperscript{[28]} found that activation energies for PE thermal decomposition decreased with decreasing average molecular weight and increased branching.

In recent years, the use of catalysts to selectively crack polymers has been investigated as a potential new waste plastics recycling method\textsuperscript{[31-34]}. Previous studies of the catalytic cracking of poly(ethylene) have shown that the molecular weight range of volatile products generated by heating PE can be greatly reduced by acid catalysts\textsuperscript{[35-41]}. A variety of solid acids and bases, as well as transition metal oxides, have been employed in catalytic cracking studies (Table III.2). Poly(ethylene) catalytic cracking products have been analyzed by several researchers. Studies of the effects of catalysts on the thermal degradation of poly(ethylene) have been performed by: contacting melted polymer with catalyst in fixed bed reactors\textsuperscript{[35-37,46,47]}; heating mixtures of polymer and catalyst powders in reaction vessels\textsuperscript{[38-41,44,45]}; and passing the volatile products of poly(ethylene) pyrolysis through reactors containing cracking catalysts\textsuperscript{[42,43]}. It is impossible to identify primary cracking products by any of these methods because of the high probability of secondary reactions. However, it has been found that acid catalysts are effective for increasing the production of volatile hydrocarbons from
Table III.1 Activation Energies for Poly(ethylene) Thermal Degradation

<table>
<thead>
<tr>
<th>Thermal Analysis Method</th>
<th>Conditions</th>
<th>$E_a$ (kcal/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>isothermal</td>
<td>295 - 360 °C in N$_2$</td>
<td>Mw$^a$: 9x10$^3$ - 23x10$^3$</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 - 70</td>
<td></td>
</tr>
<tr>
<td>isothermal</td>
<td>375 - 426 °C vacuum</td>
<td>66.1 (Mw=23000)</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>52.6 (Mw=16000)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>46.0 (Mw=11000)</td>
<td></td>
</tr>
<tr>
<td>isothermal</td>
<td>385 - 405 °C</td>
<td>Mw=20000</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>68 ($\alpha &lt; 25%$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>48 ($\alpha &gt; 25%$)</td>
<td></td>
</tr>
<tr>
<td>dynamic</td>
<td>to 500 °C @ 5 °C/min vacuum</td>
<td>Mw=20190</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48 ($\alpha &lt; 3%$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>61 (3%&lt;\alpha&lt;15%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>67 (35%&lt;\alpha&lt;95%)</td>
<td></td>
</tr>
<tr>
<td>dynamic</td>
<td>to 487 °C @ 4 and 8 °C/min in N$_2$</td>
<td>high linear PE:</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>79 (Mw=707000)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>59 (Mw=7000)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>branched PE:</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mw=54000-22000</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>55 - 39</td>
<td></td>
</tr>
<tr>
<td>dynamic</td>
<td>to 500 °C @ 10 °C/min, N$_2$: 160 ml/min</td>
<td>18.1 ($\alpha &lt; 3.4%$)</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55.4 (3.4 &lt; $\alpha &lt; 49%$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>146.6 (49 &lt; $\alpha &lt; 97%$)</td>
<td></td>
</tr>
<tr>
<td>factor-jump TG</td>
<td>410 - 475 °C</td>
<td>under vacuum:</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65.4 for both linear and branched PE in N$_2$:</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>62.5 (linear PE)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>61.2 (branched PE)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ polymer molecular weight

$^b$ percentage of decomposition reaction completed.
<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Compositions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Acids</td>
<td>Al₂O₃, SiO₂, Si-Al (13% Al₂O₃), Si-Al (20-24% Al₂O₃), Zeolites(^a)</td>
<td>35, 37-45, 47</td>
</tr>
<tr>
<td>Solid Bases</td>
<td>MgO</td>
<td>42</td>
</tr>
<tr>
<td>Transition Metal Oxides</td>
<td>ZnO, TiO₂, Cr₂O₃, Fe₂O₃, Co₃O₄, CuO, MnO₂</td>
<td>37, 42</td>
</tr>
<tr>
<td>Other</td>
<td>Activated Carbon</td>
<td>36, 42</td>
</tr>
</tbody>
</table>

\(^a\) Zeolites included: HZSM-5, HY, ReY (Re₂O₃ 10.7%), NaY, H-Theta-1, H-Mordenite.
poly(ethylene) degradation. Uemichi et al found that the relative amount of C_3-C_5 hydrocarbons derived from poly(ethylene) degradation could be increased to 70% of the polymer weight when a Si-Al catalyst was employed\textsuperscript{[35]}. They reported that poly(ethylene) catalytic cracking with a Si-Al catalyst yielded a mixture containing 57% alkanes, 34% alkenes, and 5% aromatics at 452 °C. In contrast, thermal decomposition products formed in the absence of catalysts were distributed over a wide range of carbon number and the product mixture contained 24% alkanes and 76% alkenes\textsuperscript{[35]}. Activated carbon was found to be an effective catalyst for the formation of normal alkanes in the C_1-C_5 range and for aromatics in C_6-C_8 range\textsuperscript{[36]}. Poly(ethylene) volatile products formed over activated carbon reportedly consisted of 56% alkanes, 6.3% alkenes and 37% aromatics. Simionescu et al.\textsuperscript{[37]} reported that the efficiency of several different catalysts for poly(ethylene) cracking was in the order: MnO_2 < Cr_2O_3 < CuO < Si-Al (13% Al_2O_3) < Si-Al (25% Al_2O_3) < HY zeolite. Audisio et al.\textsuperscript{[38]} used TG to study the effect of catalysts on poly(ethylene) cracking processes. They used Freeman and Carrol's method\textsuperscript{[48]} to calculate the activation energy (E_a) and reaction order (n) for the overall volatilization process (Table III.3). Their results were consistent with those reported by Simionescu et al.\textsuperscript{[37]} and reflect the facts that the acid strengths of Si-Al catalysts increase with increasing Al_2O_3 content\textsuperscript{[42,49]} and that HZSM-5 is a significantly stronger acid catalyst than amorphous Si-Al\textsuperscript{[50]}.

In order to compare the polymer cracking properties of different catalysts, it is preferable to examine the effects of catalysts without complications due to...
Table III.3 Activation Energies for Poly(ethylene) Catalytic Degradation

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_i^c$ (°C)</th>
<th>$T_m^d$ (°C)</th>
<th>$T_f^e$ (°C)</th>
<th>$E_a$ (kcal/mol)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>430</td>
<td>480</td>
<td>495</td>
<td>65.2</td>
<td>0.14</td>
</tr>
<tr>
<td>PE + Al₂O₃</td>
<td>410</td>
<td>480</td>
<td>500</td>
<td>43.5</td>
<td>0.10</td>
</tr>
<tr>
<td>PE + SiO₂</td>
<td>420</td>
<td>480</td>
<td>505</td>
<td>46.2</td>
<td>0.21</td>
</tr>
<tr>
<td>PE + HY</td>
<td>220</td>
<td>385</td>
<td>410</td>
<td>13.7</td>
<td>0.11</td>
</tr>
<tr>
<td>PE + ReY</td>
<td>220</td>
<td>390</td>
<td>410</td>
<td>9.8</td>
<td>0.08</td>
</tr>
<tr>
<td>PE + SAHAₐ</td>
<td>290</td>
<td>395</td>
<td>435</td>
<td>28.2</td>
<td>0.11</td>
</tr>
<tr>
<td>PE + SALAₐ</td>
<td>325</td>
<td>425</td>
<td>450</td>
<td>29.6</td>
<td>0.04</td>
</tr>
</tbody>
</table>

ₐ SAHA = Si-Al (Al₂O₃ 24.2%)
ₐ SAAL = Si-Al (Al₂O₃ 13.2%)

$T_i$ = temperature corresponding to a 5% weight loss

$T_m$ = temperature corresponding to the maximum rate of weight loss

$T_f$ = temperature corresponding to the final constant weight
reactions of primary cracking products with polymer residue. Secondary reactions can be minimized by limiting the contact between primary volatile products and the catalyst/polymer mixture. This can be accomplished by preparing samples with high catalyst to polymer ratios and providing efficient and rapid removal of volatile products. The focus of the studies described here was to compare the initial catalytic cracking products obtained from samples prepared by coating silica-alumina, HZSM-5, and sulfated zirconia catalysts with thin layers of poly(ethylene). From these comparisons, the effects of catalyst acidity and zeolite channel structure on volatile catalytic cracking product distributions was assessed.

III.2 Characterization of Poly(ethylene) Samples

Two poly(ethylene) polymers were used in experiments described here: a high molecular weight poly(ethylene) (HPE) (MW=8.03 x 10^4 amu, see Section II.5) from Aldrich Chemical (Milwaukee, WI) and a low molecular weight poly(ethylene) (LPE) (MW=700 amu) from Polysciences Inc. (Warrington, PA). Solid-state and liquid phase $^{13}$C-NMR, pyrolysis GC/MS, and TG-MS techniques were employed to characterize the poly(ethylene) samples.

III.2.1 $^{13}$C-NMR

Solid-state and liquid phase $^{13}$C-NMR experiments were performed for both
HPE and LPE samples. Hexamethyldisiloxane was used as an internal reference (2.0 ppm vs. tetramethylsilane) for liquid phase $^{13}$C-NMR measurements. Figures III.1 and III.2 show the solid-state $^{13}$C-NMR spectra of HPE and LPE. There is only one peak in the HPE spectrum (Figure III.1), located at 29.98 ppm, whereas Figure III.2 shows that the LPE spectrum contains three peaks located at 11.85, 21.82 and 29.98 ppm.

Whereas solid-state spectra contained very broad peaks, liquid phase $^{13}$C-NMR spectra provided more fine structure. The liquid phase $^{13}$C-NMR spectrum for HPE is shown in Figure III.3. Like the solid-state spectrum, there is only one peak, located at 29.93 ppm. This peak corresponds to the methylene carbons, suggesting that the HPE polymer had little branching. Liquid phase $^{13}$C-NMR spectra of the LPE sample are shown in Figures III.4 and III.5. Examination of the LPE spectra shows that four small peaks appear in the spectrum along with a major peak at 29.92 ppm. Two were at about the same location as those found in the solid-state spectrum. The two close to the large peak were not observed in the solid-state spectrum because the large peak in solid-state $^{13}$C-NMR was too broad. These peaks suggest that the LPE polymer is structurally different from the HPE polymer. By using the Grant and Paul approach, calculations of chemical shifts corresponding to the small peaks were made by using the formula:

$$\delta = -2.5 + \Sigma nA$$

where $\delta$ is the predicted carbon atom chemical shift; $A$ is the additive shift parameter; and $n$ is the number of carbon atoms for each shift parameter.
Figure III.1 Solid-state $^{13}$C NMR spectrum for HPE polymer.
Figure III.2 Solid-state $^{13}$C NMR spectrum for LPE polymer.
Figure III.3 Liquid phase $^{13}$C NMR spectrum for HPE polymer.
Figure III.4 Liquid phase $^{13}$C NMR spectrum for LPE polymer.
Figure III.5 Expanded view of the LPE $^{13}$C NMR spectrum shown in Figure III.4.
Calculations were performed to estimate the chemical shifts that would be found if the polymer was linear and if it contained side chain branching. Assuming that the polymer contained no side chain branching, the calculated and observed chemical shifts are given in Table III.4. The calculated and observed values for this case are in good agreement. The assignments of these small peaks suggest that these chemical shifts resulted from methyl and methylene carbons in LPE end groups:

$$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$$

Table III.4 Calculated and Observed Chemical Shifts of LPE

<table>
<thead>
<tr>
<th>Carbon Atom</th>
<th>Chemical Shifts (ppm)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Observed</td>
</tr>
<tr>
<td>C1</td>
<td>13.90</td>
<td>13.99</td>
</tr>
<tr>
<td>C2</td>
<td>23.00</td>
<td>22.81</td>
</tr>
<tr>
<td>C3</td>
<td>32.40</td>
<td>32.13</td>
</tr>
<tr>
<td>C4</td>
<td>29.90</td>
<td>29.54</td>
</tr>
<tr>
<td>C5</td>
<td>30.20</td>
<td>overlapped by major -CH\text{2}_- peak</td>
</tr>
<tr>
<td>C6</td>
<td>30.30</td>
<td>29.93, major -CH\text{2}_- peak</td>
</tr>
</tbody>
</table>

Table III.5 contains calculated chemical shifts that would be expected if the LPE polymer contained side chain branching:
In this case, CH₃ and CH chemical shifts would appear in ¹³C-NMR spectra and chemical shifts for the methylene carbon atoms located at the α, β, γ, δ and ε positions relative to the branching point would be different from those in a linear polymer. Chemical shifts would also be different for each carbon atom in the side chain.

Table III.5  Calculated ¹³C Backbone Chemical Shifts as a Function of Branch Length

<table>
<thead>
<tr>
<th>Branch Length</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>methine (br)</td>
</tr>
<tr>
<td>1</td>
<td>32.0</td>
</tr>
<tr>
<td>2</td>
<td>48.8</td>
</tr>
<tr>
<td>3</td>
<td>46.3</td>
</tr>
<tr>
<td>4</td>
<td>46.6</td>
</tr>
<tr>
<td>5</td>
<td>46.7</td>
</tr>
</tbody>
</table>

It can be seen from Table III.5 that the predicted chemical shifts for the methine and α carbon atoms would be greatly affected by branching and shift upfield. However, the LPE ¹³C-NMR spectrum did not contain peaks that could be assigned to these
chemical shifts. The likely reason the chemical shift representing end groups were observed in the LPE spectrum but not in the HPE spectrum was because the HPE chain length was much larger (ca 100x) than the LPE chain length. As a result, the end group peak intensities were below the noise level in the spectrum.

III.2.2 Pyrolysis GC/MS Results

Pyrolysis GC/MS results obtained at 400, 500, and 600 °C for the LPE and HPE polymers were compared to investigate the influences of molecular weight and pyrolysis temperature on volatile product distributions. Identification of degradation products was based on mass spectra library searches and comparisons with retention times of reference substances.

Figure III.6 shows the effect of pyrolysis temperature on neat LPE degradation. GC/MS mass spectra revealed that chromatograms consisted of repeating groups of peaks. The first elution of each grouping corresponded to a 1-alkene. The second elution of each group corresponded to an n-alkane. Close examination of chromatograms revealed the presence of small shoulders just before some alkene peaks that were due to alkadienes. Mass spectra corresponding to the peak shoulder indicated that these species had the same number of carbon atoms as the 1-alkene and n-alkane in the peak grouping. Above C_{17}, resolution of peak groupings was poor. Figure III.7 shows an example of a triplet grouping in which C_{13}^\text{\tiny --} corresponds to a thirteen carbon alkadiene, and C_{13}^\text{\tiny \tiny --} and C_{13}^\text{\tiny \tiny \tiny --} represent the
Figure III.6 Pyrolysis GC/MS chromatograms for neat LPE obtained at 400, 500 and 600 °C.
Figure III.7 Expanded view of Figure III.6 showing the formation of alkadiene, alkene and alkane.
corresponding alkene and alkane. The chromatograms in Figure III.6 are consistent with previous PE pyrolysis results reported in the literature\textsuperscript{[19,10,21,22]}. By comparing the chromatograms in Figure III.6, changes in decomposition product distributions with pyrolysis temperature can be observed. When LPE was pyrolyzed at 400 °C, decomposition products up to C\textsubscript{22} were detected. The relative yields of alkanes were larger than the corresponding alkenes except for C\textsubscript{6} hydrocarbons, for which more hexene was formed. No volatile aromatic products were detected at 400 °C. When LPE was pyrolyzed at higher temperatures, 1-alkenes became the most abundant products. Small amounts of aromatics, such as benzene and toluene, were detected at 500 and 600 °C. At the higher pyrolysis temperatures, more low molecular weight species were detected. For example, propane and propene were detected when LPE was pyrolyzed at 600 °C, but were not detected at 400 and 500 °C.

The effect of temperature on neat HPE pyrolysis is shown in Figure III.8. Volatile decomposition products with carbon numbers up to 35 were detected in this chromatogram. Pyrolysis GC/MS mass spectral library searches for PE elutions indicated that the primary products were 1-alkenes. Some of the 1-alkene chromatographic peaks were accompanied by two smaller peaks at higher temperatures, one eluting prior to the 1-alkene and another eluting after. The early eluting peak was identified as an alkadiene and the late eluting peak was identified as an alkane. When HPE was pyrolyzed at 400 °C, the pyrogram exhibited a maximum total ion current at C\textsubscript{24} - C\textsubscript{25}. C\textsubscript{6} was the only detectable product with less than 10 carbons at this temperature. When HPE was pyrolyzed at 500 °C, the
Figure III.8 Pyrolysis GC/MS chromatograms for neat HPE obtained at 400, 500 and 600 °C.
relative amounts of hydrocarbon products with less than 10 carbons were greatly increased. The 500 °C pyrogram in Figure III.8 contains three total ion current maxima at C₉, C₁₁-C₁₄, and C₂₃. A similar trend was observed for the 600 °C pyrogram.

As expected, pyrolysis GC/MS results showed that radical thermal decomposition of neat LPE and HPE produced wide ranges of hydrocarbon products. Volatile product distributions depended on the pyrolysis temperature and the initial molecular weight of the polymer. Volatile products ranged from C₃ to C₂₂ for LPE and from C₃ to C₃₅ for HPE. The fraction of low molecular weight products increased when the pyrolysis temperature was increased from 400 °C to 500 and 600 °C, suggesting the involvement of competitive secondary decomposition reactions at the higher temperatures.

### III.2.3 TG-MS Results

TG-MS weight loss curves for neat poly(ethylene) samples are shown in Figure III.9. Both LPE and HPE exhibited single step decompositions. However, the weight loss rate during decomposition was lower for LPE. The weight loss step for LPE began at about 250 °C and ended at about 450 °C. On the other hand, the weight loss step for HPE began at about 425 °C and ended at about 500 °C. These results are consistent with the report by Mucha[28] that the thermal stability of poly(ethylene) depends on the initial molecular weight of the polymer[25,28]. Figure
Figure III.9  TG-MS weight loss curves for neat LPE and HPE polymers obtained by heating samples at a rate of 10 °C/min.
III.10 shows TG-MS mass spectral ion intensities as a function of temperature for hexane, hexene and aromatics detected during TG-MS analysis of the HPE sample. The left y-axis refers to the hexene ion count and the right y-axis corresponds to the hexane and aromatic ion counts. All three profiles exhibited single step evolutions. Hexane and hexene temperature profiles were similar. Aromatics evolved at higher temperatures, suggesting that the activation energy for the formation of aromatics was greater than that for the formation of alkanes and alkenes.

III.3 Catalytic Cracking of Poly(ethylene)

Pyrolysis GC/MS and TG-MS analyses were carried out on samples containing poly(ethylene) and various catalysts to investigate the effects of different catalysts and cracking temperature on poly(ethylene) decomposition products.

III.3.1 Pyrolysis GC/MS Results

Pyrolysis GC/MS results obtained for the poly(ethylene)/catalyst samples at 400, 500, and 600 °C were compared to investigate the temperature dependence of volatile product yields. Major products consisted of alkenes, alkanes and aromatics. Alkadienes were not detected in significant quantities for any of the poly(ethylene)/catalyst samples. The effect of Si-Al catalyst on the thermal degradation of the LPE sample at different temperatures is illustrated by Figure
Figure III.10 Hexane, hexene and aromatics temperature profiles obtained from TG-MS analysis of HPE polymer.
After comparing Figure III.11 with Figure III.6, it can be seen that pyrolysis GC/MS chromatograms obtained when Si-Al catalyst was present exhibit fewer elutions after 30 min (e.g. > C₁₀). Thus, one role of the catalysts was to restrict the molecular weight range of volatile hydrocarbon products, leading primarily to the production of low molecular weight species. However, as illustrated by chromatogram differences shown in Figure III.11, the volatile product distributions for LPE/Si-Al samples obtained at the three cracking temperatures were quite different. Table III.6 lists volatile product distributions derived from chromatograms obtained at 500 and 600 °C for samples comprised of LPE coated on the Si-Al catalyst. No information regarding catalytic cracking processes at 400 °C is given for the LPE/Si-Al sample because the chromatogram obtained at this cracking temperature contained broad, overlapping peaks. Apparently, low boiling-point volatile products evolved over a relatively long time at 400 °C and therefore could not be separated. In contrast, higher boiling-point species accumulated at the column head during microfurnace cracking and therefore eluted as narrower peaks. At 500 °C, 94% of the volatile hydrocarbon products were in the C₃ to C₅ range and aromatics comprised 4% of the total volatile products. The relative amounts of alkenes were much higher than the corresponding alkanes. Mass spectral information indicated that the chromatogram contained several alkene elutions that had mass spectra containing the same molecular ion and similar fragmentation patterns, indicating that these species were isomers. Similar results were observed for alkane elutions. Figure III.12 shows an example of the formation of alkane and
Figure III.11 Pyrolysis GC/MS chromatograms for LPE/Si-Al samples obtained at 400, 500 and 600 °C.
Table III.6 Pyrolysis Products for the LPE/Si-Al Sample

<table>
<thead>
<tr>
<th>Class</th>
<th>500 °C</th>
<th>600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂-alkene</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>C₃-alkane</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>C₄-alkene</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>C₅-alkane</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>C₆-alkene</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>C₇-alkane</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>C₈-alkene</td>
<td>17</td>
<td>11</td>
</tr>
<tr>
<td>C₉-alkene</td>
<td>12</td>
<td>7</td>
</tr>
<tr>
<td>Aromatics</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Total</td>
<td>98</td>
<td>99</td>
</tr>
</tbody>
</table>

*aPercentage of integrated total ion current
bThe estimated error was ±2%
Figure III.12 Evolutions of butane and butene isomers derived from the LPE/Si-Al sample pyrolyzed at 600 °C.
alkene isomers. Mass spectra for the LPE/Si-Al pyrogram obtained at 600 °C (Figure III.12) indicated that C4 alkanes and alkenes consisted of isobutane, n-butane, isobutene, cis-butene and trans-butene isomers and evolutions of these isomers were in the order of increasing boiling-points. Two aromatic products (toluene and ethyl benzene or xylene) were detected at 500 °C. Ethyl benzene and xylenes give very similar fragmentation patterns and their boiling-points are very close. Therefore, they could not be distinguished by comparing their mass spectra. At 600 °C, a slight increase in the yield of C3 - C5 alkenes and a reduction in the yield of higher molecular weight species were observed, suggesting that primary hydrocarbon products may undergo further scission reactions at the higher temperature, resulting in the formation of lower molecular weight species. Five alkyl aromatic products were detected at 600 °C. They were toluene, ethyl benzene and/or xylene, isopropyl benzene and methylethyl benzene. Benzene was not detected at any of the cracking temperatures. Pyrograms for LPE/ZrO2/So4 samples obtained at different temperatures are shown in Figure III.13 and the effect of cracking temperature on product yields is summarized in Table III.7. Eighty-five percent of the volatile products at 400 °C were C3 - C8 alkanes or alkenes. The C3 - C5 alkane and alkene yield increased when the LPE/ZrO2/So4 sample was pyrolyzed at 500 °C. In particular, a significant increase in the C5 alkene yield from 4% to 10% was observed. Concurrently, a slight reduction in the yield of products with more than 5 carbon atoms was detected. Unlike the LPE/Si-Al sample, more alkanes were produced than the corresponding alkenes for this sample, with one
Figure III.13 Pyrolysis GC/MS chromatograms for LPE/ZrO$_2$/SO$_4$ samples obtained at 400, 500 and 600 °C.
Table III.7 Pyrolysis Products for LPE/ZrO₂/SO₄ Sample

<table>
<thead>
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<th>Class</th>
<th>400 °C</th>
<th>500 °C</th>
<th>600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
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<td>1</td>
<td>6</td>
</tr>
<tr>
<td>SO₂</td>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>C₃-alkene</td>
<td>4</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>C₄-alkane</td>
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<tr>
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<td>9</td>
</tr>
<tr>
<td>C₇-alkene</td>
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<td>10</td>
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<tr>
<td>C₈-alkane</td>
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<tr>
<td>C₉-alkene</td>
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<td>6</td>
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<tr>
<td>C₁₁-alkene</td>
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<td>1</td>
</tr>
<tr>
<td>C₁₂-alkene</td>
<td>9</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Aromatics</td>
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<td>8</td>
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<tr>
<td>Total</td>
<td>99</td>
<td>97</td>
<td>97</td>
</tr>
</tbody>
</table>

*Percentage of integrated total ion current
bThe estimated error was ±2%
exception. At 600 °C, the relative yield of C₅-alkanes was higher than that of the C₂-alkenes. A dramatic increase in CO₂ and SO₂ yields were observed at 600 °C and was indicative of the decomposition of the ZrO₂/SO₄ catalyst at this temperature. Significant yields of alkyl aromatics were detected at all three temperatures. Benzene was detected in small amounts (0.6%) at 600 °C. Pyrolysis GC/MS results for the LPE/HZSM-5 sample are shown in Figure III.14 and listed in Table III.8. Like the LPE/ZrO₂/SO₄ sample, alkane yields were higher than the corresponding alkene yields. Also, alkenes with more than 6 carbons were not detected in significant amounts. When the LPE/HZSM-5 sample was pyrolyzed at 400 °C, C₃-C₁₅ hydrocarbon products were detected. However, when the same sample was pyrolyzed at 500 and 600 °C, only C₉-C₁₀ hydrocarbon products were detected. This suggests that long chain hydrocarbon products were further cracked at the higher temperatures. Alkyl aromatics were the most abundant volatile products at all three temperatures. Unlike other LPE/catalyst samples, about 1% of the volatile products was benzene at 400 °C and benzene accounted for 2% of the volatile products at 500 and 600 °C.

Figure III.15 shows the effect of the Si-Al catalyst on the thermal degradation of the HPE polymer and the volatile product distributions derived from chromatograms obtained at 500 and 600 °C are listed in Table III.9. Like the LPE/Si-Al sample, the pyrogram obtained at 400 °C contained broad, overlapping peaks and therefore no information regarding relative volatile product yields was obtained. At 500 °C, 92% of the volatile hydrocarbon products detected were in
Figure III.14 Pyrolysis GC/MS chromatograms for LPE/HZSM-5 samples obtained at 400, 500 and 600 °C.
Table III.8 Pyrolysis Products for LPE/HZSM-5 Sample

<table>
<thead>
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<th>Class</th>
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<th>500 °C</th>
<th>600 °C</th>
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</tr>
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<td>Aromatics</td>
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<tr>
<td>Total</td>
<td>93</td>
<td>99</td>
<td>98</td>
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*Percentage of integrated total ion current

bThe estimated error was ±2%
Figure III.15 Pyrolysis GC/MS chromatograms for HPE/Si-Al samples obtained at 400, 500 and 600 °C.
Table III.9 Pyrolysis Products for the HPE/Si-Al Sample

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<tr>
<td>Total</td>
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</table>

*aPercentage of integrated total ion current
bThe estimated error was ±2%
the C$_3$ to C$_{15}$ range. Like the LPE/Si-Al sample, more alkenes were produced than the corresponding alkanes. At 600 °C, a slight reduction in the yield of low molecular weight products and an increase in the yield of high molecular weight alkenes compared to the product distribution obtained at 500 °C (C$_{11}$ and C$_{12}$ in particular) suggests that contributions to volatile products from non-catalytic thermal degradation processes were greater at the higher temperature. Aromatics were not detected in significant amounts at 500 and 600 °C. Pyrolysis GC/MS volatile product distributions for the HPE/ZrO$_2$/SO$_4$ sample are shown in Figure III.16 and listed in Table III.10. Unlike the LPE/ZrO$_2$/SO$_4$ sample, the relative amounts of alkanes were less than that of the corresponding alkenes at all three temperatures. Eighty percent of the volatile products at 500 °C were C$_3$-C$_{13}$ alkenes and alkanes. The yields of C$_3$-C$_8$ alkanes and C$_4$ alkenes decreased significantly with increasing microfurnace temperature. Like the LPE/Si-Al sample, aromatic products were not detected in significant amounts at the three cracking temperatures. A dramatic increase in CO$_2$ yield was observed at 600 °C, and was attributed to catalyst decomposition. For the HPE/HZSM-5 sample (Figure III.17 and Table III.11), 81% of the volatile products at 400 °C were assigned to C$_2$-C$_7$ alkenes and alkanes and 9% of the volatile products were found to be aromatics. Unlike the LPE/HZSM-5 sample, the relative yield of alkanes were less than that of the corresponding alkenes. The ethylene yield increased with pyrolysis temperature whereas the yield of C$_4$ alkanes detected decreased substantially. Perhaps the most significant volatile product distribution change with temperature involved the
Figure III.16 Pyrolysis GC/MS chromatograms for HPE/ZrO₂/SO₄ samples obtained at 400, 500 and 600 °C.
Table III.10 Pyrolysis Products for the HPE/ZrO₂/SO₄ Sample

<table>
<thead>
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<th>Class</th>
<th>400°C</th>
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<th>600°C</th>
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<tr>
<td>Total</td>
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<td>96</td>
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*Percentage of integrated total ion current

b The estimated error was ±2%
Figure III.17 Pyrolysis GC/MS chromatograms for HPE/HZSM-5 samples obtained at 400, 500 and 600 °C.
Table III.11 Pyrolysis Products for the HPE/HZSM-5 Sample

<table>
<thead>
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<td>propene</td>
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<td>9</td>
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<tr>
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</tr>
<tr>
<td>Aromatics</td>
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<td>18</td>
<td>7</td>
</tr>
<tr>
<td>Total</td>
<td>92</td>
<td>96</td>
<td>92</td>
</tr>
</tbody>
</table>

*aPercentage of integrated total ion current
bThe estimated error was ±2%
fraction of aromatics formed. The proportion of aromatics formed at 500 °C was about twice that detected at 400 °C but the proportion of aromatics detected at 600 °C was less than that found at 400 °C, suggesting that there was an optimum temperature for aromatization.

Pyrolysis GC/MS results indicated that the relative yields of alkanes were greater than those of the corresponding alkenes for LPE/ZrO₂/SO₄ and LPE/HZSM-5 samples. In contrast, the relative yields of alkenes were greater than those of the corresponding alkanes for all other polymer/catalyst samples. Also, the relative yields of aromatics were greater for the LPE/catalyst samples than the corresponding HPE/catalyst samples. Because LPE and HPE differ only in chain length, these volatile product differences can be attributed to polymer molecular weight differences.

III.3.3 TG-MS Results

The thermal properties of LPE and HPE in the presence of catalysts were compared by means of TG-MS analysis so that the evolution of volatile catalytic cracking products could be correlated with sample weight loss and so that volatilization activation energies could be calculated from TG weight loss information. Weight loss curves obtained by heating samples at 10 °C/min in He are shown in Figures III.18 and III.19. The left y-axes in Figures III.18 and III.19 refer to the neat poly(ethylene) weight loss curves (solid line) and the right y-axes
Figure III.18 TG-MS weight loss curves for neat LPE and LPE/catalyst samples obtained by heating samples at a rate of 10 °C/min.
Figure III.19 TG-MS weight loss curves for neat HPE and HPE/catalyst samples obtained by heating samples at a rate of 10 °C/min.
correspond to the polymer/catalyst samples. Compared to neat polymer thermal decompositions, all three catalysts lowered the temperature at which significant sample weight loss occurred. Weight loss curves shown in Figures III.18 and III.19 exhibit a gradual decrease in sample mass above 450 °C for samples containing the Si-Al catalyst. Mass spectrometric analysis of species evolved above 450 °C revealed that this weight loss was due to loss of water from the catalyst. Similar weight loss rates were observed when neat Si-Al catalyst was analyzed by TG-MS (Section II.8). The weight loss curves for the polymer/ZrO₂/SO₄ samples exhibit two distinct steps. TG effluent mass spectra confirmed that the low temperature weight loss step was caused by poly(ethylene) decomposition. The high temperature step, which occurred above 500 °C for LPE/ZrO₂/SO₄ and above 400 °C for HPE/ZrO₂/SO₄, resulted from catalyst decomposition. Figure III.20 shows ion signal temperature profiles corresponding to total ion current, SO₂ and CO₂ obtained from TG-MS analysis of HPE/ZrO₂/SO₄. The total ion current (solid line) exhibits a doublet around 200 °C followed by a smaller peak at 500 °C. The doublet near 200 °C indicates that HPE/ZrO₂/SO₄ catalytic cracking consisted of two steps. Selected ion temperature profiles indicated that the high temperature total ion current peak corresponded to SO₂ (m/z 64) and CO₂ (m/z 44) evolutions and that the SO₂ peak maximum occurred before that for CO₂.

Figures III.21 - III.34 show TG-MS class-specific mass spectral ion signal temperature profiles for alkanes, alkenes and aromatics for the poly(ethylene)/catalyst samples. Molecular ions were selected to represent alkane and alkene
Figure III.20 TIC and ion signal temperature profiles form SO$_2$ and CO$_2$ derived from TG-MS analysis of the HPE/ZrO$_2$/SO$_4$ samples.
profiles, and the tropylium ion ($C_7H_7^+$, m/z 91), which is representative of alkyl aromatics, was selected for aromatic profiles. Ion signals shown in these figures were scaled so that the maximum ion signal for the most abundant alkene detected during TG-MS analysis of each poly(ethylene)/catalyst sample was 100%. Figures III.21 - III.22 show TG-MS class-specific mass spectral ion intensities for alkanes and alkenes as a function of temperature for the LPE/Si-Al sample. Alkenes comprised the majority of volatile products for the poly(ethylene)/silica-alumina sample and alkenes and alkanes evolved in two steps (Figures III.21 - III.22). Most volatile hydrocarbon products were produced during the second evolution. The maximum rates of alkane and alkene evolution occurred at about 390 °C. The relative yield of the most abundant alkane was about 5% of the yield of most abundant alkene. Figures III.23 - III.24 show ion signal temperature profiles representing TG-MS evolution of alkanes and alkenes for the LPE/ZrO$_2$/SO$_4$ sample. The temperature corresponding to the start of volatile product evolution for this sample was about 100 °C. Unlike TG-MS results obtained for the LPE/Si-Al sample, the ion signal temperature profiles contained only one evolution step. Like the LPE/Si-Al sample, C$_4$ alkenes were the most abundant products. The relative yield of C$_4$ alkanes, the most abundant alkane products, was about 9.5% of the C$_4$ alkenes yield. Class-specific temperature profiles for the LPE/HZSM-5 sample are shown in Figures III.25 - III.26. Like the LPE/Si-Al sample, the major volatile products formed in the presence of the zeolite catalyst were alkenes and alkanes. Also, alkanes and alkenes evolved in two steps. Unlike other LPE/catalyst samples, propene was the most
Figure III.21 Alkane temperature profiles from TG-MS analysis of the LPE/Si-Al sample.
Figure III.22 Alkene temperature profiles from TG-MS analysis of the LPE/Si-Al sample.
Figure III.23 Alkane temperature profiles from TG-MS analysis of the LPE/ZrO₂/SO₄ sample.
Figure III.24 Alkene temperature profiles from TG-MS analysis of the LPE/ZrO$_2$/SO$_4$ sample.
Figure III.25 Alkane temperature profiles from TG-MS analysis of the LPE/HZSM-5 sample.
Figure III.26 Alkene temperature profiles from TG-MS analysis of the LPE/HZSM-5 sample.
abundant product. The relative yield of the most abundant alkane (C₄) product was about 7% of that of the propene yield. The temperature corresponding to the start of volatile product evolutions was about 125 °C. Volatile product evolutions from the LPE/HZSM-5 sample started and ended at lower temperature than the LPE/Si-Al sample but at higher temperature than the LPE/ZrO₂/SO₄ sample. Figure III.27 contains m/z 91 (i.e. tropylium ion) temperature profiles for the three LPE/catalyst samples. The LPE/HZSM-5 sample produced the largest relative yield of aromatics. The benzene temperature profile was similar to that for the alkyl aromatics for the LPE/HZSM-5 sample and the relative yield of benzene was about 5% of that of the most abundant alkene production. Very little benzene was detected for the LPE/Si-Al and LPE/ZrO₂/SO₄ samples.

Figures III.28 - III.29 show TG-MS class-specific mass spectral ion signal temperature profiles for the HPE/Si-Al sample. Like the LPE/Si-Al sample, alkenes comprised the majority of volatile products and alkenes and alkanes evolved in two distinct steps. The yield of the most abundant alkane products (C₄) was about 3.2% of the most abundant alkene yield. Ion signals characteristic of alkanes exhibited maxima at 275 and 425 °C whereas ion signals representing alkenes exhibited maxima at 320 and 425 °C. Figures III.30 and III.31 show ion signal temperature profiles representing TG-MS evolution of alkenes and alkanes for the HPE/ZrO₂/SO₄ sample. The start and end temperatures corresponding to volatile product evolution for this sample were lower than those for the HPE/Si-Al sample, which started at about 125 °C. Like the HPE/Si-Al sample, two steps were evident in the ion signal
Figure 11.27 m/z 91 ion signal temperature profiles derived from TG-MS analysis of the LPE/catalyst samples.
Figure III.28 Alkane temperature profiles from TG-MS analysis of the HPE/Si-Al sample.
Figure III.29 Alkene temperature profiles from TG-MS analysis of the HPE/Si-Al sample.
Figure III.30 Alkane temperature profiles from TG-MS analysis of the HPE/ZrO$_2$/SO$_4$ sample.
Figure III.31 Alkene temperature profiles from TG-MS analysis of the HPE/ZrO₂/SO₄ sample.
temperature profiles. This result is consistent with the total ion current temperature profile shown in Figure III.20. The rate of alkane formation reached maxima at 200 °C and 240 °C whereas the rate of alkene formation exhibited maxima at 200 and 250 °C. Unlike the LPE/ZrO₂/SO₄ sample, propene was the most abundant product. The relative yield of the most abundant alkanes (C₄) was about 8% of the propene yield. Class-specific temperature profiles for the HPE/HZSM-5 sample are shown in Figures III.32 - III.33. Like the LPE/HZSM-5 sample, alkenes and alkanes were the major volatile products and alkanes and alkenes evolved in two steps. The relative yield of the most abundant alkanes was about 5% of that of the most abundant alkene products. The maximum rate of alkane formation occurred at 200 °C whereas the maximum rate of alkene formation occurred at 270 °C. Temperatures corresponding to the start and end of volatile product evolution for this sample were similar to those for the HPE/ZrO₂/SO₄ sample. Unlike the LPE/HZSM-5 sample, C₄ alkenes rather than propene were the most abundant products. Figure III.34 contains m/z 91 temperature profiles for the three HPE/catalyst samples. Like the LPE/catalyst samples, the HPE/HZSM-5 sample yielded the largest fraction of aromatics.

Compared to neat poly(ethylene) (LPE and HPE), the decrease in the temperatures corresponding to the onset of weight loss for samples containing catalysts may be attributed to lower activation energies for acid catalyzed cracking than for free radical thermal cracking processes. Neat poly(ethylene) and the poly(ethylene)/catalyst samples were subjected to TG-MS analysis in helium (50
Figure III.32 Alkane temperature profiles from TG-MS analysis of the HPE/HZSM-5 sample.
Figure III.33 Alkene temperature profiles from TG-MS analysis of the HPE/HZSM-5 sample.
Figure 111.34 m/z 91 ion signal temperature profiles derived from TG-MS analysis of the HPE/catalyst samples.
ml/min) with heating rates of 1, 10, 25 and 50°C/min to investigate the effects of catalysts on volatilization and class-specific activation energies. TG-MS weight loss data obtained by using different heating rates were used to calculate volatilization activation energies by using the method described by Friedman\cite{55}. Volatilization activation energies calculated from the TG-MS information are given in Table III.12. The highest volatilization activation energies were obtained for the neat polymer samples, and the activation energy for the neat HPE polymer was higher than that for the LPE polymer. This result is consistent with TG measurements (Figure III.9), in which the weight loss onset temperature was about 170 °C higher for the HPE polymer than for the LPE polymer. The lowest volatilization activation energies were obtained for samples containing the ZrO\textsubscript{2}/SO\textsubscript{4} catalyst, which was the strongest acid catalyst of those employed in this study. For samples containing the same catalyst, those containing the LPE polymer exhibited a lower volatilization activation energy than those containing HPE polymer. However, this difference was statistically significant only for samples containing the ZrO\textsubscript{2}/SO\textsubscript{4} catalyst, for which there was a 5 kcal/mol difference. The volatilization activation energies listed in Table III.12 are very different from those reported by Audisio et al\cite{38}. However, Audisio et al did not report a PE molecular weight and error estimates for their values, which were obtained from single TG measurements by using the Freeman and Carrol method\cite{48}, were not given. The activation energy error estimates reported here were standard deviations derived from four separate TG measurements for each sample.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>LPE</th>
<th>HPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>40 ± 1</td>
<td>59 ± 1</td>
</tr>
<tr>
<td>Si-Al</td>
<td>37 ± 2</td>
<td>37 ± 3</td>
</tr>
<tr>
<td>ZrO$_2$/SO$_4$</td>
<td>23 ± 2</td>
<td>28 ± 2</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>27 ± 4</td>
<td>31 ± 1</td>
</tr>
</tbody>
</table>
Class-specific activation energies were calculated from the TG-MS mass spectral information by using the technique of linear programmed thermal degradation mass spectrometry\(^{56}\) and are listed in Tables III.13 and III.14. Class-specific activation energies increased with decreasing catalyst acidity for both LPE/catalyst and HPE/catalyst samples. For samples containing the same catalyst, those containing the LPE polymer exhibited lower class-specific activation energies than those containing HPE polymer. These results are consistent with the volatilization activation energies obtained from TG measurements. However, different techniques and calculation methods resulted in differences between volatilization activation energies and class-specific activation energies.

### III.4 Discussion

The primary products detected in this study are not the same as those previously reported for the catalytic cracking of poly(ethylene)\(^{35-47}\). The primary low temperature volatile products reported in previous work were isoalkanes whereas isoalkenes were the primary products detected in this study. Figures III.21 - III.34 indicate that \(C_4\) alkenes were the most abundant volatile products detected during TG-MS analysis of the LPE/Si-Al, LPE/ZrO\(_2\)/SO\(_4\), HPE/Si-Al, and HPE/HZSM-5 samples and that propene was the most abundant volatile product for the LPE/HZSM-5 and HPE/ZrO\(_2\)/SO\(_4\) samples. Pyrolysis-GC/MS results confirmed that the most abundant \(C_4\) alkene isomer produced by catalytically cracking
Table III.13  TG-MS Class-specific Activation Energies (kcal/mol) for LPE/Catalyst Samples

<table>
<thead>
<tr>
<th>Class</th>
<th>LPE/Si-Al</th>
<th>LPE/HZSM-5</th>
<th>LPE/ZrO&lt;sub&gt;2&lt;/sub&gt;/SO&lt;sub&gt;4&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propene</td>
<td>30 ± 1</td>
<td>27 ± 1</td>
<td>19 ± 1</td>
</tr>
<tr>
<td>C&lt;sub&gt;4&lt;/sub&gt;-Alkenes</td>
<td>30 ± 4</td>
<td>29 ± 1</td>
<td>20 ± 1</td>
</tr>
<tr>
<td>C&lt;sub&gt;4&lt;/sub&gt;-Alkanes</td>
<td>29 ± 2</td>
<td>25 ± 2</td>
<td>19 ± 1</td>
</tr>
<tr>
<td>C&lt;sub&gt;5&lt;/sub&gt;-Alkenes</td>
<td>31 ± 2</td>
<td>29 ± 1</td>
<td>20 ± 1</td>
</tr>
<tr>
<td>C&lt;sub&gt;5&lt;/sub&gt;-Alkanes</td>
<td>29 ± 2</td>
<td>24 ± 1</td>
<td>19 ± 1</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;-Alkenes</td>
<td>29 ± 1</td>
<td>27 ± 1</td>
<td>21 ± 1</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;-Alkanes</td>
<td>29 ± 3</td>
<td>24 ± 1</td>
<td>20 ± 1</td>
</tr>
<tr>
<td>C&lt;sub&gt;7&lt;/sub&gt;-Alkenes</td>
<td>30 ± 3</td>
<td></td>
<td>20 ± 1</td>
</tr>
<tr>
<td>C&lt;sub&gt;7&lt;/sub&gt;-Alkanes</td>
<td>30 ± 3</td>
<td></td>
<td>20 ± 1</td>
</tr>
<tr>
<td>Aromatics</td>
<td>38 ± 5</td>
<td>24 ± 2</td>
<td>20 ± 3</td>
</tr>
</tbody>
</table>
Table III.14 TG-MS Class-specific Activation Energies (kcal/mol) for HPE/Catalyst Samples

<table>
<thead>
<tr>
<th>Class</th>
<th>PE/Si-Al</th>
<th>PE/HZSM-5</th>
<th>PE/ZrO$_2$/SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propene</td>
<td>38 ± 1</td>
<td>34 ± 2</td>
<td>19 ± 1</td>
</tr>
<tr>
<td>C$_4$-Alkenes</td>
<td>43 ± 2</td>
<td>30 ± 1</td>
<td>23 ± 1</td>
</tr>
<tr>
<td>C$_4$-Alkanes</td>
<td>42 ± 3</td>
<td>26 ± 1</td>
<td>23 ± 1</td>
</tr>
<tr>
<td>C$_5$-Alkenes</td>
<td>39 ± 1</td>
<td>29 ± 1</td>
<td>22 ± 1</td>
</tr>
<tr>
<td>C$_5$-Alkanes</td>
<td>36 ± 2</td>
<td>28 ± 2</td>
<td>22 ± 1</td>
</tr>
<tr>
<td>C$_6$-Alkenes</td>
<td>38 ± 2</td>
<td></td>
<td>23 ± 1</td>
</tr>
<tr>
<td>C$_6$-Alkanes</td>
<td>35 ± 4</td>
<td></td>
<td>22 ± 1</td>
</tr>
<tr>
<td>C$_7$-Alkenes</td>
<td>34 ± 3</td>
<td></td>
<td>23 ± 1</td>
</tr>
<tr>
<td>C$_8$-Alkenes</td>
<td>38 ± 3</td>
<td></td>
<td>23 ± 1</td>
</tr>
<tr>
<td>C$_9$-Alkenes</td>
<td>43 ± 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aromatics</td>
<td></td>
<td></td>
<td>29 ± 1</td>
</tr>
</tbody>
</table>
poly(ethylene) was isobutene. The carbenium ion model for catalytic cracking\(^{57,58}\) can be used to explain the formation of the most abundant volatile products. During poly(ethylene) cracking, protons from Brønsted acid catalysts can attack polymer chains resulting in chain shortening and the formation of primary carbenium ions.

\[
R'\text{-CH}_2\text{-CH}_2\text{-R}^* \xrightarrow{H^+} R'\text{-CH}_2 + \text{CH}_3\text{-R}^* \tag{23}
\]

Primary carbenium ions can react via inter- or intra-molecular mechanisms to produce secondary carbenium ions, which may rearrange to form more stable tertiary ions.

\[
R'\text{-CH}_2 + R''\text{-CH}_2\text{-R}'' \rightarrow R'\text{-CH}\text{-R}'' + R'\text{-CH}_3 \tag{24}
\]

\[
\begin{array}{c}
R'\text{-CH}_2\text{-CH}\text{-R}^* \\
\text{management}
\end{array} \rightarrow \begin{array}{c}
R'\text{-C}\text{-R}^* \\
\text{CH}_3
\end{array} \tag{25}
\]

Beta-scissions of these secondary and tertiary carbenium ions can result in the formation of new primary carbenium ions and chain end olefins.

\[
\begin{array}{c}
R'\text{-CH}_2\text{-C}\text{-R}^* \\
\text{R}
\end{array} \xrightarrow{\beta\text{-scission}} \begin{array}{c}
R'\text{-C}\text{-R}^* \\
\text{R}
\end{array} + \begin{array}{c}
\text{CH}_2\text{-C}\text{-R}'' \\
\text{R}
\end{array} \tag{26}
\]
Chain end olefin double bonds can react with catalyst protons to again form carbenium ions, which, after \( \beta \)-scission can produce propene or isobutene, depending on whether \( R \) in the equation below is H or CH\(_3\).

\[
\begin{align*}
\text{CH}_2\text{C}-\text{R}^* & \xrightarrow{H^+} \text{CH}_3\text{C}-\text{R}^* \\
\text{CH}_3\text{C}=\text{C}-\text{CH}_3-\text{R}' & \xrightarrow{\beta \text{-scission}} \text{CH}_3\text{C}=\text{CH}_2 + \text{R}'\text{°} 
\end{align*}
\]  \hspace{1cm} (27)

Tertiary carbenium ions formed in reaction (27) may also undergo hydride abstraction from the polymer residue to produce propane or isobutane, depending on whether \( R \) is H or CH\(_3\).

\[
\begin{align*}
\text{CH}_3\text{C}-\text{R}^* & \xrightarrow{\text{H}^\text{°}} \text{CH}_3\text{CH}-\text{R}^* 
\end{align*}
\]  \hspace{1cm} (28)

The formation of all other alkanes and alkenes can be represented by a similar series of reactions when \( R \) and \( R' \) represent different groups (such as ethyl, propyl, etc). Class-specific temperature profiles shown in Figures III.21 - III.26 and III.28 - III.33 clearly show that alkane and alkene production occurred in two steps for all poly(ethylene)/catalyst samples except for the LPE/ZrO\(_2\)/SO\(_4\) sample. From these TG-MS temperature profiles, it can be found that the maximum rate of volatile
product formation for first step occurred at about 255 °C for the LPE/Si-Al sample but at about 155 °C for the LPE/HZSM-5 sample. The maximum rate of volatile product formation for the second step occurred at 380 °C for the LPE/Si-Al sample, and at 230 °C for the LPE/HZSM-5 sample. The maximum rate of volatile product formation for the LPE/ZrO$_2$/SO$_4$ sample occurred at 195 °C. For the HPE/catalyst samples, the maximum rate of volatile product formation for the first step occurred at about 320 °C for the sample containing the Si-Al catalyst but at about 200 °C for samples containing the higher acidity HZSM-5 and sulfated zirconia catalysts. The maximum rate of volatile product formation for the second step occurred at 425 °C for the HPE/Si-Al sample, at 270 °C for the HPE/HZSM-5 sample, and at 250 °C for the HPE/ZrO$_2$/SO$_4$ sample. The general trend was that the rate of product formation in the second stage maximized at lower temperatures for the higher acidity catalysts.

The formation of aromatics is thought to be due to oligomerization of olefins in the reacting mixture$^{[49,59,60]}$. Cyclization of these olefins can occur when a six-member ring can be formed and these rings rapidly dehydrogenate to produce aromatics. However, cyclization may involve other reactions in addition to 1,6-ring closure.
Because all three polymer/catalyst samples exhibited two stage cracking mechanisms, the two steps were most likely due to heterogeneity in the poly(ethylene). The first stage of volatile product formation may result from catalyst protons attacking polymer defect groups such as internal or terminal double bonds\cite{58} which may be too few to be detected by $^{13}$C NMR. The second step may reflect the acid catalyzed cracking of the -CH$_2$- polymer backbone.

Figures III.27 and III.34 and volatile product distribution tables indicate that the HZSM-5 catalyst was particularly effective at forming aromatics. One difference between this catalyst and the others was that HZSM-5 had a crystalline structure containing two intersecting channels\cite{61}. One HZSM-5 channel is straight and has a nearly circular opening (0.54 nm x 0.56 nm) and the other channel is sinusoidal and somewhat more elliptical (0.51 nm x 0.56 nm). The acid sites of HZSM-5 are located within these channels. Therefore, acid catalyzed reactions occur within a restricted volume. The fact that aromatics were detected only after significant
quantities of alkenes were observed suggests that aromatics were formed by alkene cyclization reactions. Due to the restricted HZSM-5 channel volume, oligomerization reactions resulted in the efficient formation of small alkyl aromatics, such as toluene, xylene, isopropyl benzene and indane.

After comparing the TG-MS weight loss curves for the poly(ethylene)/ZrO$_2$/SO$_4$ samples (Figures III.18 and III.19) with hydrocarbon class temperature profiles (Figures III.25 - III.26 and Figures III.32 - III.33), it can be seen that the weight loss steps that occurred at higher temperatures for these samples did not result in the formation of hydrocarbon products. Mass spectra obtained during this high temperature weight loss step indicated that the primary volatile products were SO$_2$ and CO$_2$. Thus, the sulfated zirconia catalyst decomposed at high temperature. However, under identical TG-MS analysis conditions but in the absence of polymer, no SO$_2$ evolution was detected and the sulfated zirconia catalyst was found to be stable to 600 °C. Apparently, species formed near the sulfated zirconia acid site during poly(ethylene) cracking were responsible for making the catalyst thermally unstable below 600 °C. The TG-MS temperature profiles for m/z 64 (SO$_2$) and m/z 44 (CO$_2$) shown in Figure III.20 indicate that SO$_2$ evolution preceded CO$_2$ evolution. This is consistent with a sulfated zirconia decomposition mechanism in which SO$_3$ surface species decomposes to SO$_2$ and oxygen atoms.[62]

$$\text{SO}_3 \rightarrow \text{SO}_2 + \text{O}$$
In the absence of adsorbates, individual oxygen atoms eventually combine to produce O₂. However, when organics are present on the catalyst surface (e.g. polymer residue), oxygen atoms can react to ultimately form CO₂. Consequently, CO₂ evolution was detected after SO₂ evolution. As shown in Figures III.18 and III.19, poly(ethylene)/Si-Al TG-MS weight loss curves exhibited a gradual weight loss process. Unlike other poly(ethylene)/catalyst samples, catalytic cracking processes for poly(ethylene)/Si-Al samples were slow and incomplete at 400 °C. TG-MS weight loss ended at 450 and 475 °C for the LPE/Si-Al and HPE/Si-Al samples, respectively. Therefore, it is understandable that pyrolysis GC/MS chromatograms obtained at 400 °C contained broad and overlapping peaks for poly(ethylene)/Si-Al samples.

III.5 CONCLUSIONS

The molecular weight range of the volatile cracking products derived from LPE and HPE was narrower when catalysts were employed. Volatile product distributions were affected by the choice of catalyst as well as the cracking conditions. A fewer number of catalytic cracking products would be preferred for tertiary recycling because this simplifies subsequent isolation steps required to recover chemicals from plastic wastes. The fact that the catalytic cracking products obtained by TG-MS were not the same as those derived from pyrolysis GC/MS suggests that cracking processes were significantly affected by sample heating rates.
The heating rate was much faster for pyrolysis GC/MS analyses than for TG-MS analyses. Pyrolysis GC/MS and TG-MS results indicated that poly(ethylene) thermal stability was dependent on the polymer initial molecular weight. The difference between thermal cracking volatilization activation energies for LPE and HPE was about 19 kcal/mol, whereas when catalysts were present, the difference was less than 5 kcal/mol. This indicates that radical thermal cracking reactions are more dependent on the initial PE molecular weight than catalytic cracking reactions. Compared to thermal cracking, catalysts dramatically reduced the volatilization activation energies for PE thermal decomposition, which may directly lead to a reduction in energy, and therefore operational cost, required for processing plastic wastes by using a catalytic cracking tertiary recycling process.
III.6 References


Chapter IV
Catalytic Cracking of Poly(styrene)

IV.1 Background

Poly(styrene) was first introduced as a commercial plastic in 1930\textsuperscript{[11]}. Since then, it has been used in a wide array of everyday items, ranging from disposable beverage cups and food packaging to appliances, electronics and automobile components. Because of its versatility and low production costs, poly(styrene) has become a popular choice with engineers and product designers. Of the 68 billion pounds of poly(styrene) produced in the United States each year, about 1 billion pounds are used in single-use disposable applications\textsuperscript{[2]}.

The thermal degradation of poly(styrene) was first studied in 1935\textsuperscript{[3]}, and has been the subject of numerous studies since then\textsuperscript{[4-12]}. The chemical nature of the volatile products, the rate of evolution of volatile products, and the molecular weight changes in the residue are three degradation aspects studied by researchers. Mechanistic studies of poly(styrene) thermal degradation prior to 1986 was reviewed by Guyot\textsuperscript{[10]}, and a comprehensive list of the thermal degradation products was recently published by McNeill et al\textsuperscript{[11]}. Between 200 and 300°C, poly(styrene)
degradation takes place without the evolution of volatile products, and only a decrease of the polymer molecular weight is observed\textsuperscript{10,11,13}. At higher temperatures, both molecular weight decreases and evolution of volatile products occur. Volatile products detected at higher temperature comprise mainly styrene monomer, dimer and trimer and a small amount of other low molecular weight species such as toluene and $\alpha$-methyl styrene.

The reduction of poly(styrene) molecular weight at low temperature is a result of random C-C chain scission (reaction 1) and disproportionation (reaction 2) of the resulting macroradicals.

\begin{equation}
\begin{align*}
\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 & \rightarrow \text{CH}_3-\text{CH} \quad (A) \\
& + \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 \quad (B)
\end{align*}
\end{equation}

\begin{equation}
\begin{align*}
\text{CH}_2-\text{CH}_2 & \quad (C) \\
& + \text{CH}_2-\text{CH}-\text{CH}_2-\text{CH} \quad (D)
\end{align*}
\end{equation}

Because no volatile products are produced below 300°C, it may be concluded that neither (A) nor (B) radicals undergo appreciable depolymerization and chain ends (C) and (D) that are formed in reaction 2 are stable in this temperature region\textsuperscript{10,11}.

At higher temperatures, macroradical (A) has been shown to undergo several competing reactions:

(1) unzipping to produce monomer:
(2) intramolecular hydrogen transfer (back biting) to form styrene dimer or trimer fragments:

Six dimer isomers with relative yields greater than 0.1% were reported in the literature\textsuperscript{[14]}: 2,4-diphenyl-1-butene, 1,2-diphenyl-2-butene, 1,2-diphenyl-1-butene, 1,4-diphenyl-1-butene, 3,4-diphenyl-1-butene, and 1,4-diphenyl-2-butene. Five trimer isomers with relative yields greater than 0.1% were reported by the same authors. Two of these trimers were 2,4,6-triphenyl-1-hexene and 1,2,6-triphenyl-3-hexene. The other isomer structures were not identified. Among the dimer and trimer isomers, 1,2-diphenyl-1-butene (19%) and 2,4,6-triphenyl-1-hexene (9.2%) were found in greatest yields when poly(styrene) was decomposed at 300 °C.

(3) intermolecular hydrogen transfer:
Macroradical (E) may undergo $\beta$-scission to form macroradical (A) and an unsaturated chain end.

The behavior of macroradical (B) may be described by the following reactions:

1. disproportionation with macroradical (A):

2. $\beta$-scission:

3. intramolecular hydrogen transfer followed by $\beta$-scission:
At temperatures above 300° C, macromolecules (C) and (D) may undergo homolytic cleavage. The random scission of (C) and (D) would be similar to reaction (1). It has been reported that a C-C bond located in position β to an unsaturated chain end is more thermally unstable than the other bonds in the polymer\textsuperscript{6,15}. Scission at the chain end of macromolecule (D) has been proposed to give a macroradical (A) and a substituted allyl radical, which yields α-methyl styrene after hydrogen abstraction\textsuperscript{6,16}.

Costa et al\textsuperscript{6} pointed out that scission of macromolecule (C) at the chain end should be favored relative to scission at internal bonds due to the higher mobility of toluyl
radicals, which prevents cage effect recombination of the two radicals formed by scission\[^{[6, 17]}\]:

\[
\begin{align*}
\text{(C)} & \quad \rightarrow \quad \text{(F)} + \quad \text{(B)} \\
\end{align*}
\]

Toluene may be formed from (F) by two routes. The first is disproportionation of radicals (F) and (B).

\[
\begin{align*}
\text{(F)} + \quad \text{(B)} & \quad \rightarrow \quad \text{(F)} + \quad \text{(D)} \\
\end{align*}
\]

The second is hydrogen abstraction from a neighboring poly(styrene) chain.

\[
\begin{align*}
\text{(F)} + \quad \text{(B)} & \quad \rightarrow \quad \text{(F)} + \quad \text{(D)} \\
\end{align*}
\]

The volatile product composition resulting from poly(styrene) degradation has been studied by various research groups\[^{[6,9,18-20]}\]. These studies were performed under varying conditions, including atmospheric pressure, vacuum, and a broad range of reaction temperatures, times and initial sample masses. This has led to a
range of reported product yields and kinetic parameters. There is general agreement that styrene monomer is the principal volatile product, for which yields of between 40 to 60% have been reported. Other major products include styrene dimer (ca. 10%) and trimer (ca. 20%). Toluene (1-2%) and α-methyl styrene (ca. 0.5%) are also produced. The volatilization activation energy for poly(styrene) thermal degradation has also been calculated\(^5,12,21-29\), and results of these studies are summarized in Table IV.1.

In contrast to the great efforts that have been made to investigate poly(styrene) thermal degradation, relatively few studies have focussed on the catalytic cracking of poly(styrene)\(^{20,28,30-32}\). In most of those studies, catalysts were employed to reform volatile thermal degradation products that had been generated by radical thermal degradation processes\(^{20,30-32}\). Only one study was focused on producing volatile products by direct cracking of polymer chains\(^{28}\). A variety of solid acids and bases, as well as transition metal oxides, have been employed in catalytic cracking reactions (Table IV.2). Poly(styrene) catalytic cracking products have been analyzed by several researchers. In the presence of solid acid catalysts, benzene was found to be a major product (ca. 35 - 53\%)\(^{28,30}\), whereas when basic catalysts and transition metal oxides were employed, styrene was the major product (ca. 70\%)\(^{30}\). Simionescu et al.\(^{31}\) reported that the efficiency of catalysts for poly(styrene) cracking was in the order: \(\text{MnO}_2 < \text{Cr}_2\text{O}_3 < \text{CuO} < \text{Si-Al (13\% Al}_2\text{O}_3)\) < \(\text{Si-Al (25\% Al}_2\text{O}_3) < \text{HY}\). Audisio et al.\(^{28}\) used TG to study the effects of catalysts on poly(styrene) cracking processes. They used Freeman and Carrol's
<table>
<thead>
<tr>
<th>Thermal Analysis Method</th>
<th>Conditions</th>
<th>$E_a$(kcal/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>isothermal</td>
<td>348° - 398°C vacuum</td>
<td>44.7</td>
<td>21</td>
</tr>
<tr>
<td>isothermal</td>
<td>335° - 365°C vacuum</td>
<td>54 - 58</td>
<td>22</td>
</tr>
<tr>
<td>dynamic</td>
<td>to 500°C @ 5°C/min vacuum</td>
<td>61 ($\alpha^* &lt; 15%$) 67 ($\alpha &gt; 35%$)</td>
<td>23</td>
</tr>
<tr>
<td>isothermal</td>
<td>&lt; 353°C vacuum</td>
<td>49</td>
<td>5</td>
</tr>
<tr>
<td>isothermal</td>
<td>260° - 290°C vacuum</td>
<td>43.1</td>
<td>24</td>
</tr>
<tr>
<td>dynamic</td>
<td>to 450°C @ 40°C/min N$_2$ 20 ml/min</td>
<td>33 - 55.3</td>
<td>25</td>
</tr>
<tr>
<td>isothermal</td>
<td>350° - 450°C vacuum and N$_2$</td>
<td>45</td>
<td>26</td>
</tr>
<tr>
<td>isothermal</td>
<td>350° - 420°C vacuum</td>
<td>44.3</td>
<td>27</td>
</tr>
<tr>
<td>dynamic</td>
<td>to 600°C @ 20°C/min N$_2$ 50 ml/min</td>
<td>66.3</td>
<td>28</td>
</tr>
<tr>
<td>isothermal</td>
<td>330° - 410°C</td>
<td>46.7</td>
<td>29</td>
</tr>
<tr>
<td>isothermal</td>
<td>370° - 420°C N$_2$ 5 ml/min</td>
<td>39.8</td>
<td>12</td>
</tr>
</tbody>
</table>

*percentage of reaction completed.
Table IV.2 Catalysts Used in Previous Studies

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Compositions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Acids</td>
<td>SiO$_2$, Al$_2$O$_3$, Si-Al (13% Al$_2$O$_3$), Si-Al (24% Al$_2$O$_3$), HY$^{a}$, ReY$^{b}$</td>
<td>20, 28, 30</td>
</tr>
<tr>
<td>Solid Bases</td>
<td>MgO, CaO, BaO, K$_2$O</td>
<td>32</td>
</tr>
<tr>
<td>Transition Metal Oxides</td>
<td>TiO$_2$, Cr$_2$O$_3$, Fe$_2$O$_3$, Co$_3$O$_4$, CuO, ZnO, MnO$_2$</td>
<td>31, 32</td>
</tr>
</tbody>
</table>

$^a$HY = H-Y zeolite

$^b$ReY = Re-Y zeolite (Re$_2$O$_3$ 10.7%)
method\cite{33} to calculate the activation energy ($E_a$) and reaction order ($n$) for the overall process (Table IV.3). In contrast to the results reported by Simionescu et al.\cite{31}, they found that the activation energy for a low $\text{Al}_2\text{O}_3$ content Si-Al catalyst was lower than that for a high $\text{Al}_2\text{O}_3$ content Si-Al catalyst. Audisio et al. reported that low and high $\text{Al}_2\text{O}_3$ content Si-Al catalysts were more active than the HY and ReY zeolites, which was also inconsistent with results reported by Simionescu et al. In addition, Audisio's results were inconsistent with the facts that the number of active sites and the acid strengths of Si-Al catalysts increase with increasing $\text{Al}_2\text{O}_3$ content\cite{34,35}, and that HZSM-5 is a significantly stronger acid catalyst than amorphous Si-Al\cite{36}. One goal of the studies described here was to resolve the literature discrepancies regarding catalyst activity for poly(styrene) cracking.

**IV.2 Characterization of Poly(styrene) Samples**

Two poly(styrene) polymers were used in experiments described here: a high molecular weight poly(styrene) (HPS) (MW=850,000 amu), and a low molecular weight poly(styrene) (LPS) (MW=2,700 amu). Both were purchased from Aldrich Chemical (Milwaukee, WI). Structure information for these polymers provided by Aldrich\cite{37} indicated that the end groups for the HPS polymer were styrene, whereas end groups for the LPS polymer were butyl and styrene.
Table IV.3 Activation Energies for Poly(styrene) Catalytic Degradation

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_i^c$ (°C)</th>
<th>$T_m^d$ (°C)</th>
<th>$T_f^e$ (°C)</th>
<th>$E_a$ (kcal/mol)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>355</td>
<td>425</td>
<td>460</td>
<td>66.3</td>
<td>0.63</td>
</tr>
<tr>
<td>PS + Al$_2$O$_3$</td>
<td>340</td>
<td>430</td>
<td>460</td>
<td>36.2</td>
<td>0.24</td>
</tr>
<tr>
<td>PS + SiO$_2$</td>
<td>350</td>
<td>430</td>
<td>470</td>
<td>39.4</td>
<td>0.27</td>
</tr>
<tr>
<td>PS + HY</td>
<td>270</td>
<td>420</td>
<td>450</td>
<td>23.0</td>
<td>0.33</td>
</tr>
<tr>
<td>PS + ReY</td>
<td>300</td>
<td>430</td>
<td>455</td>
<td>27.2</td>
<td>0.38</td>
</tr>
<tr>
<td>PS + SAHA$^a$</td>
<td>290</td>
<td>380</td>
<td>415</td>
<td>14.8</td>
<td>0.21</td>
</tr>
<tr>
<td>PS + SALA$^b$</td>
<td>275</td>
<td>375</td>
<td>415</td>
<td>10.9</td>
<td>0.16</td>
</tr>
</tbody>
</table>

$^a$ SAHA = Si-Al (Al$_2$O$_3$ 24.2%)

$^b$ SALA = Si-Al (Al$_2$O$_3$ 13.2%)

$^c$ $T_i$ = temperature corresponding to a 5% weight loss

$^d$ $T_m$ = temperature corresponding to the maximum rate of weight loss

$^e$ $T_f$ = temperature corresponding to the final constant weight
$^{13}$C-NMR, pyrolysis GC-MS, and TG-MS techniques were employed to characterize the poly(styrene) samples.

IV.2.1 $^{13}$C-NMR

Liquid phase $^{13}$C-NMR experiments were performed at 90 °C for both HPS and LPS samples. Hexamethyldisiloxane was used as an internal reference (2.0 ppm vs. tetramethylsilane)\textsuperscript{[38]}. The $^{13}$C-NMR spectrum for the HPS sample is shown in Figure IV.1. This spectrum is almost identical to that reported by Randall\textsuperscript{[39]}, which implies that the HPS had a structure that was similar to Randall's poly(styrene) sample. The poly(styrene) sample used to obtained his spectrum was made by free radical polymerization. The aromatic ring carbons produced resonances ranging from 123 to 144 ppm, whereas methylene and methine groups gave resonances at 41-42 and 39.2 ppm, respectively. Randall concluded that his spectrum represented poly(styrene) with a structure that is syndiotactic with styrene as end groups. The fact that the spectrum in Figure IV.1 is similar to that published by Randall suggests that the HPS polymer had styrene end groups, which was confirmed by the HPS supplier\textsuperscript{[37]}.

The $^{12}$C NMR spectrum of the LPS sample is shown in Figures IV.2 and IV.3. Examination the LPS spectrum shows that all major peaks are located at the same positions as those in HPS sample spectrum, but several small peaks appear between 12-37 ppm in the spectrum. This finding confirms that the LPS polymer had
Figure IV.2 Liquid phase $^{13}$C NMR spectrum for LPS polymer.
Figure IV.3 Expanded view of the LPS $^{13}$C NMR spectrum shown in Figure IV.2.
different end groups than the HPS polymer. By using the Grant and Paul approach[^40] and aromatic substituent parameters[^39], calculations of chemical shifts corresponding to the small peaks were made by using the formula[^40,^41]:

$$ \delta = -2.5 + \Sigma nA $$

where $\delta$ is the predicted chemical shift for a carbon atom; $A$ is the additive shift parameter; and $n$ is the number of carbon atoms for each shift parameter. Calculated and observed chemical shifts are given in Table IV.4. The calculated values agree well with the observed. These chemical shifts correspond to an LPS structure with n-butyl end groups:
Table IV.4 Calculated and Observed Chemical Shifts of LPS

<table>
<thead>
<tr>
<th>Carbon Atom</th>
<th>Chemical Shifts (ppm)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Observed</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>11.80</td>
<td>12.07</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>20.89</td>
<td>20.69</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>30.29</td>
<td>30.04 - 30.10</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>25.51</td>
<td>25.16 - 25.26</td>
<td></td>
</tr>
<tr>
<td>C5</td>
<td>35.60</td>
<td>35.67 - 36.10</td>
<td></td>
</tr>
</tbody>
</table>

The presence of aromatic rings resulted in peak splitting, giving multiple peaks for C3, C4 and C5. The LPS NMR spectrum is consistent with the claim made by the manufacturer that this polymer contained n-butyl and styrene end groups.

IV.2.2 Pyrolysis GC/MS Results

Pyrolysis GC-MS results obtained at 400, 500, and 600 °C for the LPS and HPS polymers were compared to investigate the influences of molecular weight, different end groups, and pyrolysis temperature on volatile product distributions. The identification of the degradation products was based on mass spectra library search, as well as retention times and mass spectra of reference substances. The
following pure substances were used as references: benzene, toluene, ethyl benzene, m-, o-, and p-xylenes, styrene, α-methyl styrene, indane, indene, naphthalene, 1-methyl naphthalene, 2-methyl naphthalene, 1,2,4-trimethyl benzene, 1,2,4,5-tetramethyl benzene, 1,3,5-triisopropyl benzene, and cyclopropyl benzene. These pure substances were divided into four groups according to their boiling points. Reference samples were made by mixing 100 µl of each pure substance in each group. If there was no retention time and mass spectrum match between samples and references, the reference substance was assumed not to be present in the decomposition or cracking products.

Figure IV.4 shows the effect of pyrolysis temperature on neat LPS polymer degradation. At higher pyrolysis temperatures, more degradation products appear in chromatograms. Table IV.5 contains the volatile product distributions derived from LPS pyrolysis at 400, 500 and 600 °C. Only those degradation products that were formed in amounts greater than 1% are listed in product tables. The products listed in Table IV.5 represented at least 91% of the detected volatile products. The styrene yield increased from 41% to about 62% when the pyrolysis temperature was increased from 400 to 600 °C. Two styrene dimer isomers were detected at 400 °C and three dimers were detected at 500 and 600 °C. Only one styrene trimer was detected at all three temperatures. The sum of styrene dimer yields is listed in the product table (Table IV.5). The total styrene dimer yield dropped from 15% to 11% when the pyrolysis temperature was increased from 400 to 500 °C, but remained the same when the pyrolysis temperature was increased to 600 °C. The
Figure IV.4 Pyrolysis GC/MS chromatograms for neat LPS obtained at 400, 500 and 600 °C.
Table IV.5 Pyrolysis Products from Neat Low Molecular Weight Poly(styrene)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Relative Abundance (%)&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 °C</td>
</tr>
<tr>
<td>benzene</td>
<td>3</td>
</tr>
<tr>
<td>toluene</td>
<td>1</td>
</tr>
<tr>
<td>ethyl benzene</td>
<td>2</td>
</tr>
<tr>
<td>styrene</td>
<td>41</td>
</tr>
<tr>
<td>methyl styrene</td>
<td>1</td>
</tr>
<tr>
<td>methyl indane</td>
<td>2</td>
</tr>
<tr>
<td>dimer</td>
<td>15</td>
</tr>
<tr>
<td>trimer</td>
<td>35</td>
</tr>
<tr>
<td>Total</td>
<td>92</td>
</tr>
</tbody>
</table>

<sup>a</sup> Percentage of integrated total ion current  
<sup>b</sup>The estimated error was ±2%
styrene trimer yield decreased dramatically from 35% to 3% when the pyrolysis temperature was increased from 400 to 600 °C. This is consistent with previous reports that the thermally labile trimer easily decomposes to form monomer and other minor products at high reaction temperatures\(^{19}\). Minor products that were detected at high temperatures included: benzene, toluene, ethyl benzene and \(\alpha\)-methyl styrene. The yields of these minor products increased with increased pyrolysis temperature. Small amounts of butane were detected at 500 and 600 °C and pentene was detected at 600 °C. The relative yields of butane and pentene were less than 1% and therefore are not listed in Table IV.5.

The effect of temperature on neat HPS polymer pyrolysis is shown in Figure IV.5 and product distributions for neat HPS sample pyrolysis obtained at different temperatures are given in Table IV.6. It can be seen that the styrene yield dropped slightly from 68% to 66% when the pyrolysis temperature was increased from 400 to 500 °C, but remained approximately the same when the temperature was raised to 600 °C. Unlike the LPS sample, three styrene dimer isomers and two trimer isomers were detected at all temperatures. The total styrene dimer yield increased slightly (9% to 11%) with increasing pyrolysis temperature. The total styrene trimer yield decreased from 21% to 15% when the pyrolysis temperature was increased from 400 to 500 °C, and dropped significantly (to 3%) when the pyrolysis temperature was increased to 600 °C. Like the LPS sample, several minor products were detected at 500 and 600 °C. No alkane or alkene products were detected at any of the three temperatures.
Figure IV.5 Pyrolysis GC/MS chromatograms for neat HPS obtained at 400, 500 and 600 °C.
Table IV.6 Pyrolysis Products from Neat High Molecular Weight Poly(styrene)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Relative Abundance (%)&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 °C</td>
</tr>
<tr>
<td>benzene</td>
<td>3</td>
</tr>
<tr>
<td>toluene</td>
<td>1</td>
</tr>
<tr>
<td>ethyl benzene</td>
<td>3</td>
</tr>
<tr>
<td>styrene</td>
<td>68</td>
</tr>
<tr>
<td>methyl styrene</td>
<td>1</td>
</tr>
<tr>
<td>methyl indene</td>
<td>1</td>
</tr>
<tr>
<td>dimer</td>
<td>9</td>
</tr>
<tr>
<td>trimer</td>
<td>21</td>
</tr>
<tr>
<td>Total</td>
<td>98</td>
</tr>
</tbody>
</table>

<sup>a</sup> Percentage of integrated total ion current

<sup>b</sup>The estimated error was ±2%
Pyrolysis GC/MS results show that radical thermal decomposition of neat HPS and LPS polymer samples produced large quantities of styrene and chain end back biting yielded substantial amounts of styrene dimer and trimer. The dimer and trimer yields decreased and the yields of several minor products increased when the pyrolysis temperature was increased to 600 °C, suggesting the involvement of competitive secondary reactions at higher temperatures. Although the product yields for the HPS and LPS samples were different, both samples yielded the same volatile products. Only small amounts of butene and pentene, which were not detected for the HPS samples, were detected when LPS samples were pyrolyzed at 500 and 600 °C, which may result from the cleavage of bonds at butyl chain ends. It can therefore be concluded that poly(styrene) thermal degradation mechanisms were not significantly affected by the initial polymer molecular weight or the chemical structure of chain ends that were present in the two polymers. These results are consistent with those reported in literature[6,9].

IV.2.3 TG-MS Results

TG-MS weight loss curves for neat poly(styrene) samples were only slightly different (Figure IV.6). The weight loss step began about 25°C earlier for the LPS sample than for the HPS sample. However, the weight loss rate during decomposition was lower for the LPS sample. These results are consistent with those reported by McNeill et al[11]. Those authors proposed that the initial weight
Figure IV.6 TG-MS weight loss curves for neat LPS and HPS polymers obtained by heating samples at a rate of 10 °C/min.
loss temperature was dependent on the concentration of chain ends, which was higher for the low molecular weight poly(styrene) sample. Figure IV.7 shows TG-MS mass spectral ion intensities as a function of temperature for styrene monomer, dimer, and trimer detected during TG-MS analysis of neat LPS sample. The left y-axis represents the monomer evolution, and the right y-axis is for the dimer and trimer evolutions. All three products exhibited single step evolutions and evolved simultaneously during the TG-MS analysis. These results indicate that competing reactions (3) and (4) occurred simultaneously. Similar results were observed for the HPS sample.

Pyrolysis GC/MS and TG-MS results indicate that the complexity of the degradation processes increases with increasing pyrolysis temperature, and that the polymer thermal stability is dependent on the initial molecular weight. The major products for both poly(styrene) samples were: monomer, dimer, and trimer.

IV.3 Catalytic Cracking of Poly(styrene)

Pyrolysis GC/MS, TG-MS and TG-GC/MS experiments were carried out on samples containing poly(styrene) and various catalysts to examine the effects of different catalysts and temperatures on poly(styrene) cracking.
Figure IV.7  Styrene monomer, dimer and trimer temperature profiles derived from TG-MS analysis of the neat LPS sample.
IV.3.1 Pyrolysis GC/MS Results

Pyrolysis GC/MS results obtained for the poly(styrene)/catalyst samples at 400, 500, and 600 °C were compared to investigate the temperature dependence of volatile product yields. The effect of Si-Al catalyst on the thermal degradation of the LPS sample at different temperatures is illustrated in Figure IV.8. Compared to neat poly(styrene) thermal degradation product distributions, the presence of catalyst increased the number of different volatile products detected. Table IV.7 contains the volatile product distributions derived from chromatograms obtained at 400, 500, and 600 °C for LPS/Si-Al samples. The products listed in this table comprised over 90% of the detected volatile products. Unlike neat polymer samples, benzene was the most abundant volatile product at all three pyrolysis temperatures. The benzene yield remained fairly constant (27 - 33%) for pyrolysis at 400, 500, and 600 °C. Other volatile products detected in substantial yield at the three pyrolysis temperatures included: alkyl benzenes, indanes, indenes and naphthalenes. Trace amounts of propene were detected when LPS/Si-Al samples were pyrolyzed at 500 and 600 °C. The styrene yield was about 1% at 400 °C, but rose dramatically to 12% at 600 °C. This suggests that contributions to volatile products from thermal cracking were greater at higher pyrolysis temperatures. Pyrograms for LPS/ZrO₂/SO₄ samples obtained at different temperatures are shown in Figure IV.9 and the effect of temperature on product yields is given in Table IV.8. Like the LPS/Si-Al samples, benzene was the major catalytic cracking product. Unlike the
Figure IV.8 Pyrolysis GC/MS chromatograms for LPS/Si-Al samples obtained at 400, 500 and 600 °C.
Table IV.7 Pyrolysis Products from the LPS/Si-Al Sample

<table>
<thead>
<tr>
<th>Substance</th>
<th>Relative Abundance (%)&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 °C</td>
</tr>
<tr>
<td>benzene</td>
<td>31</td>
</tr>
<tr>
<td>toluene</td>
<td>1</td>
</tr>
<tr>
<td>ethyl benzene</td>
<td>20</td>
</tr>
<tr>
<td>styrene</td>
<td>1</td>
</tr>
<tr>
<td>isopropyl benzene</td>
<td>6</td>
</tr>
<tr>
<td>methyl styrene</td>
<td></td>
</tr>
<tr>
<td>indane</td>
<td>10</td>
</tr>
<tr>
<td>indene</td>
<td>1</td>
</tr>
<tr>
<td>methyl indane</td>
<td>17</td>
</tr>
<tr>
<td>methyl indene</td>
<td></td>
</tr>
<tr>
<td>naphthalene</td>
<td>4</td>
</tr>
<tr>
<td>methyl naphthalene</td>
<td>6</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>97</td>
</tr>
</tbody>
</table>

<sup>a</sup> Percentage of integrated total ion current

<sup>b</sup>The estimated error was ±2%
Figure IV.9 Pyrolysis GC/MS chromatograms for LPS/ZrO₂/SO₄ samples obtained at 400, 500 and 600 °C.
Table IV.8 Pyrolysis Products from the LPS/ZrO$_2$/SO$_4$ Sample

<table>
<thead>
<tr>
<th>Substance</th>
<th>Relative Abundance (%)$^{a,b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 °C</td>
</tr>
<tr>
<td>CO$_2$</td>
<td></td>
</tr>
<tr>
<td>SO$_2$</td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>31</td>
</tr>
<tr>
<td>toluene</td>
<td>1</td>
</tr>
<tr>
<td>ethyl benzene</td>
<td>10</td>
</tr>
<tr>
<td>isopropyl benzene</td>
<td>6</td>
</tr>
<tr>
<td>indane</td>
<td>10</td>
</tr>
<tr>
<td>methyl indane</td>
<td>25</td>
</tr>
<tr>
<td>dimethyl indane</td>
<td>3</td>
</tr>
<tr>
<td>naphthalene</td>
<td>2</td>
</tr>
<tr>
<td>methyl naphthalene</td>
<td>4</td>
</tr>
<tr>
<td>Total</td>
<td>92</td>
</tr>
</tbody>
</table>

$^a$ Percentage of integrated total ion current

$^b$ The estimated error was ±2%
LPS/Si-Al samples, indanes were the next most important products at 400 °C, followed by alkyl benzenes and naphthalenes. Comparable amounts of benzene and indanes were generated from LPS/Si-Al and LPS/ZrO₂/SO₄ samples when they were pyrolyzed at 400 °C. Styrene and indenes, which were detected when LPS/Si-Al samples were pyrolyzed, were not detected at any pyrolysis temperature for the LPS/ZrO₂/SO₄ samples. Propene, butane and pentane were detected in small amounts at 400 °C. However, only pentane was detected at 500 and 600 °C. Figure IV.8 shows that two peaks appeared in the 600 °C pyrogram at retention times between 2 to 4 minutes. Mass spectral library search indicated that these two peaks corresponded to CO₂ and SO₂ evolutions. These products were likely formed by the decomposition of the ZrO₂/SO₄ catalyst[42]. Like the LPS/Si-Al and LPS/ZrO₂/SO₄ samples, benzene was the most abundant catalytic cracking product for the LPS/HZSM-5 sample (Figure IV.10 and Table IV.9). The benzene yield at 400 °C was over 50% for this sample. The relative yields of ethyl benzene and indanes were much less for the LPS/HZSM-5 samples than for the LPS/Si-Al and LPS/ZrO₂/SO₄ samples. Unlike the products derived from the other catalysts, no isopropyl benzene was detected for LPS/HZSM-5 samples. However, significant quantities of indenes were detected at all three pyrolysis temperatures. Small amounts of xylenes, which were not detected in LPS/Si-Al and LPS/ZrO₂/SO₄ samples, were also detected at 500 and 600 °C. Propene and butene were detected in small amounts when LPS/HZSM-5 samples were pyrolyzed at 500 and 600 °C.

Figure IV.11 shows the effect of the Si-Al catalyst on the thermal degradation
Figure IV.10 Pyrolysis GC/MS chromatograms for LPS/HZSM-5 samples obtained at 400, 500 and 600 °C.
Table IV.9 Pyrolysis Products from the LPS/HZSM-5 Sample

<table>
<thead>
<tr>
<th>Substance</th>
<th>Relative Abundance (%)&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 °C</td>
</tr>
<tr>
<td>benzene</td>
<td>52</td>
</tr>
<tr>
<td>toluene</td>
<td>3</td>
</tr>
<tr>
<td>ethyl benzene</td>
<td>5</td>
</tr>
<tr>
<td>xylene</td>
<td></td>
</tr>
<tr>
<td>styrene</td>
<td>1</td>
</tr>
<tr>
<td>methyl styrene</td>
<td></td>
</tr>
<tr>
<td>indane</td>
<td>7</td>
</tr>
<tr>
<td>indene</td>
<td>3</td>
</tr>
<tr>
<td>methyl indane</td>
<td>7</td>
</tr>
<tr>
<td>methyl indene</td>
<td>3</td>
</tr>
<tr>
<td>naphthalene</td>
<td>7</td>
</tr>
<tr>
<td>methyl naphthalene</td>
<td>6</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>94</strong></td>
</tr>
</tbody>
</table>

<sup>a</sup> Percentage of integrated total ion current

<sup>b</sup>The estimated error was ±2%
Figure IV.11 Pyrolysis GC/MS chromatograms for HPS/Si-Al samples obtained at 400, 500 and 600 °C.
of the HPS polymer. At 400 and 500 °C, benzene was the most abundant volatile product (Table IV.10). The benzene yield decreased with increasing pyrolysis temperature but styrene and ethyl benzene yields increased. The indanes yield also decreased significantly with increasing pyrolysis temperature from over 15% at 400 °C to 1% at 600 °C. Unlike LPS/Si-Al samples, styrene was the most abundant product (30%) at 600 °C, followed by ethyl benzene and benzene. Small amounts of propene were detected at 600 °C. Comparable amounts of benzene were produced from the LPS/Si-Al and HPS/Si-Al samples at 400 °C. However, benzene yield for the HPS/Si-Al sample at 600 °C was about half of that detected for the LPS/Si-Al sample, whereas the relative yields of ethyl benzene and styrene were about twice as much as those detected for the LPS/Si-Al sample at 600 °C. Pyrolysis GC/MS volatile product distributions for the HPS/ZrO$_2$/SO$_4$ sample are shown in Figure IV.12 and listed in Table IV.11. Benzene was again the most abundant product. Propene was detected at all three temperatures. Comparable amounts of benzene were produced from the HPS/Si-Al and HPS/ZrO$_2$/SO$_4$ samples when they were pyrolyzed at 400 °C, but the yields of indanes detected from the HPS/ZrO$_2$/SO$_4$ sample were much less than those for the HPS/Si-Al sample at 400 °C. Unlike the LPS/ZrO$_2$/SO$_4$ sample, a 2% styrene yield was detected at 500 and 600 °C and a small amount of indene was detected at 600 °C. The methyl indane yield was only about one-third of that detected for the LPS/ZrO$_2$/SO$_4$ sample at 400 °C. Like the LPS/ZrO$_2$/SO$_4$ sample, CO$_2$ and SO$_2$ were detected when the HPS/ZrO$_2$/SO$_4$ sample was pyrolyzed. For the HPS/HZSM-5 sample (Figure IV.13
Table IV.10 Pyrolysis Products from the HPS/Si-Al Sample

<table>
<thead>
<tr>
<th>Substance</th>
<th>Relative Abundance (%)&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 °C</td>
</tr>
<tr>
<td>benzene</td>
<td>31</td>
</tr>
<tr>
<td>toluene</td>
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</tr>
<tr>
<td>ethyl benzene</td>
<td>14</td>
</tr>
<tr>
<td>styrene</td>
<td>4</td>
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<td>4</td>
</tr>
<tr>
<td>indane</td>
<td>15</td>
</tr>
<tr>
<td>indene</td>
<td>5</td>
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<tr>
<td>methyl indane</td>
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</tr>
<tr>
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<td>2</td>
</tr>
<tr>
<td>naphthalene</td>
<td>3</td>
</tr>
<tr>
<td>methyl naphthalene</td>
<td>4</td>
</tr>
<tr>
<td>Total</td>
<td>98</td>
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<sup>a</sup> Percentage of integrated total ion current

<sup>b</sup>The estimated error was ±2%
Figure IV.12 Pyrolysis GC/MS chromatograms for HPS/ZrO₂/SO₄ samples obtained at 400, 500 and 600 °C.
<table>
<thead>
<tr>
<th>Substance</th>
<th>Relative Abundance (%)&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 °C</td>
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<tr>
<td>CO₂</td>
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</tr>
<tr>
<td>SO₂</td>
<td></td>
</tr>
<tr>
<td>propene</td>
<td>1</td>
</tr>
<tr>
<td>benzene</td>
<td>33</td>
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<td>ethyl benzene</td>
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<td>indene</td>
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<td>Total</td>
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<sup>a</sup> Percentage of integrated total ion current

<sup>b</sup> The estimated error was ±2%
Figure IV.13 Pyrolysis GC/MS chromatograms for HPS/HZSM-5 samples obtained at 400, 500 and 600 °C.
and Table IV.12), the yield of benzene was about 60% at the 400 °C pyrolysis temperature, but dropped to about 30% when the HPS/HZSM-5 sample was pyrolyzed at 500 and 600 °C. Unlike the HPS/Si-Al and HPS/ZrO₂/SO₄ samples, small amounts of xylenes were detected for the HPS/HZSM-5 sample at all three temperatures. Unlike the LPS/HZSM-5 sample, no dramatic changes in styrene yield were observed at different pyrolysis temperatures. The styrene yield was about 2% at 400 °C and about 8% at 600 °C. However, the styrene yield was about 1% at 400 °C but 13% at 600 °C for the LPS/HZSM-5 sample. Small amounts of propene were detected at all three pyrolysis temperatures. Pyrolysis GC/MS results indicate that the relative yields of alkyl benzenes were the greatest for the LPS and HPS samples containing Si-Al and ZrO₂/SO₄ catalysts. In contrast, samples containing HZSM-5 catalyst produced fewer alkyl benzenes but significantly larger quantities of indenes. The similarities between results for LPS and HPS suggest that the formation of volatile cracking products were not significantly affected by the polymer end group differences.

IV.3.2 TG-MS Results

TG-MS was employed to correlate the evolution of volatile catalytic cracking products with sample weight loss and to calculate volatilization activation energies. Weight loss curves obtained by heating samples at 10 °C/min in He are shown in Figures IV.14 and IV.15. The left y-axes in Figures IV.14 and IV.15 refer to the neat
### Table IV.12 Pyrolysis Products from the HPS/HZSM-5 Sample

<table>
<thead>
<tr>
<th>Substance</th>
<th>Relative Abundance (%)&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 °C</td>
</tr>
<tr>
<td>benzene</td>
<td>60</td>
</tr>
<tr>
<td>toluene</td>
<td>2</td>
</tr>
<tr>
<td>ethyl benzene</td>
<td>2</td>
</tr>
<tr>
<td>xylene</td>
<td></td>
</tr>
<tr>
<td>styrene</td>
<td>2</td>
</tr>
<tr>
<td>methyl styrene</td>
<td>1</td>
</tr>
<tr>
<td>indane</td>
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</tr>
<tr>
<td>indene</td>
<td>3</td>
</tr>
<tr>
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<tr>
<td>naphthalene</td>
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</tr>
<tr>
<td>methyl naphthalene</td>
<td>4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>91</td>
</tr>
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</table>

<sup>a</sup> Percentage of integrated total ion current

<sup>b</sup>The estimated error was ±2%
Figure IV.14 TG-MS weight loss curves for neat LPS and LPS/catalyst samples obtained by heating samples at a rate of 10 °C/min.
Figure IV.15 TG-MS weight loss curves for neat HPS and HPS/catalyst samples obtained by heating samples at a rate of 10 °C/min.
poly(styrene) weight loss curves (solid lines) and the right y-axes correspond to the polymer/catalyst samples. Compared to neat polymer thermal decompositions (Figure IV.6), all three catalysts lowered the temperature at which significant sample weight loss occurred. The catalytic effect was greatest for the samples containing the ZrO_2/So_4 catalyst. Comparing the curves in Figures IV.14 and IV.15 reveals that, for the same catalysts, the weight loss onset temperature was lower for the LPS polymer than for the HPS polymer. A similar result was observed for neat polymers. Weight loss curves shown in Figures IV.14 and IV.15 exhibit a gradual decrease in sample mass above 400 °C for samples containing the Si-Al catalyst. Mass spectrometric analysis of species evolved above 400 °C revealed that this weight loss was due to loss of water from the catalyst. Similar weight loss rates were observed when neat Si-Al catalyst was analyzed by TG-MS. The weight loss curves for the polymer/ZrO_2/So_4 samples exhibit two distinct steps. TG effluent mass spectra confirmed that the low temperature weight loss step was caused by poly(styrene) decomposition. The high temperature step, which occurred above 450 °C, resulted from catalyst decomposition and corresponded to SO_2 and CO_2 evolution. This was similar to what was observed for poly(ethylene)/ZrO_2/So_4 cracking (Figures III.18 and III.19).

Multiple TG-MS analyses with different sample heating rates were performed to obtain volatilization activation energies by using the Friedman technique^{43}. Volatilization activation energies calculated from the TG-MS information are given in Table IV.13. The highest volatilization activation energies were obtained for the
<table>
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<th>Catalyst</th>
<th>LPS</th>
<th>HPS</th>
</tr>
</thead>
<tbody>
<tr>
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<td>$46 \pm 1$</td>
<td>$49 \pm 9$</td>
</tr>
<tr>
<td>Si-Al</td>
<td>$34 \pm 1$</td>
<td>$39 \pm 1$</td>
</tr>
<tr>
<td>ZrO$_2$/SO$_4$</td>
<td>$24 \pm 3$</td>
<td>$29 \pm 2$</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>$35 \pm 1$</td>
<td>$36 \pm 1$</td>
</tr>
</tbody>
</table>
neat polymer samples, and the activation energy for the neat HPS polymer was slightly higher than that for the neat LPS polymer. This result is consistent with TG measurements (Figure IV.6), in which the weight loss onset temperature was higher for the HPS polymer during decomposition than for the LPS polymer. The lowest volatilization activation energies were calculated for samples containing the ZrO$_2$/SO$_4$ catalyst, which was the strongest acid catalyst of those employed in this study. For samples containing the same catalyst, those containing the LPS polymer exhibited a lower volatilization activation energy than those containing the HPS polymer. The neat poly(styrene) activation energies listed in Table IV.13 are in agreement with previously published values$^{[5]}$. Conversely, the polymer/Si-Al volatilization activation energies listed in Table IV.13 are very different from those reported by Audisio et al$^{[28]}$. However, Audisio et al. provided no error estimates for their values, which were obtained from single measurements by using the Freeman and Carrol$^{[33]}$ method. The activation energy error estimates reported here were standard deviations derived from four separate TG measurements for each sample.

IV.3.3 TG-GC/MS Results

Mass spectra obtained during TG-MS analyses could not be used to profile the temperature dependent evolutions of the primary volatile catalytic cracking products because species specific ions could not be identified. By placing a gas
chromatograph between the thermogravimetric analyzer and mass spectrometer, it was possible to separate the primary volatile species produced in the thermogravimetric analyzer prior to mass analysis. Figure IV.16 shows an example of a TG-GC/MS chromatogram for the HPS/ZrO₂/SO₄ sample. In this figure, total ion current is plotted as a function of the TG temperature at which GC injections were made. This plot contains 31 separate chromatograms obtained during one TG weight loss analysis. Figure IV.17 shows one complete chromatogram obtained when TG effluent was injected when the TG sample was 235 °C. All of the major cracking products detected at 400 °C by pyrolysis GC/MS (Tables IV.7 - IV.12) were detected by TG-GC/MS. However, TG-GC/MS sensitivity was poorer than the pyrolysis GC/MS sensitivity because the TG He purge significantly diluted product mixtures prior to injection into the gas chromatograph. As a result, minor volatile products detected by pyrolysis GC/MS at 400 °C were not detected by TG-GC/MS.

In addition, because TG-GC/MS separations were performed isothermally and with a shorter column, the chromatographic resolution obtained by TG-GC/MS was inferior to that obtained by pyrolysis GC/MS. Despite these limitations, chromatographic peak areas representing the yields of the most abundant thermal decomposition products were obtained after deconvoluting overlapping elutions in TG-GC/MS chromatograms by using curvefitting. Figures IV.18 to IV.23 contain plots of TG-GC/MS chromatographic peak areas (integrated total ion current) as a function of sample temperature for benzene and other major products evolved from polymer/catalyst samples in TG-GC/MS experiments. The left y-axis represents
Figure IV.16 TG-GC/MS temperature profile for HPS/ZrO$_2$/SO$_4$ sample obtained by heating a sample at a rate of 5 °C/min.
Figure IV.17 Expanded view of Figure IV.16 showing one chromatogram. TG effluent injected at 235 °C.
Figure IV.18  TG-GC/MS chromatographic peak area derived from LPS/Si-Al sample decomposition as a function of the TG sample temperature.
Figure IV.19  TG-GC/MS chromatographic peak area derived from LPS/ZrO₂/SO₄ sample decomposition as a function of the TG sample temperature.
Figure IV.20  TG-GC/MS chromatographic peak area derived from LPS/HZSM-5 sample decomposition as a function of the TG sample temperature.
Figure IV.21 TG-GC/MS chromatographic peak area derived from HPS/Si-Al sample decomposition as a function of the TG sample temperature.
Figure IV.22 TG-GC/MS chromatographic peak area derived from HPS/ZrO$_2$/SO$_4$ sample decomposition as a function of the TG sample temperature.
Figure IV.23 TG-GC/MS chromatographic peak area derived from HPS/HZSM-5 sample decomposition as a function of the TG sample temperature.
benzene peak areas and the right y-axis represents all other peak areas. Comparing
results for polymer/catalyst samples reveals that volatile products began to evolve
at the lowest temperatures for samples containing $\text{ZrO}_2/\text{SO}_4$ and at the highest
temperatures when samples contained Si-Al catalyst. For all samples analyzed,
benzene was by far the most abundant volatile product. All of the polymer/catalyst
samples produced alkyl benzenes and indanes, however samples containing HZSM-5
catalyst generated significantly less than the other samples. Figures IV.18 to IV.23
show that significant quantities of benzene were detected at temperatures well
below those at which the other volatile products were detected. In addition, volatile
product yields obtained by TG-GC/MS were not the same as those derived from
pyrolysis GC/MS analyses at 400 °C, suggesting that decomposition pathways that
dominated when samples were rapidly heated to 400 °C were less important when
samples were heated at the much lower rates employed for TG analysis.

IV.4 Discussion

Formation of the primary poly(styrene) catalytic cracking volatile products
can be explained by consequences of initial electrophilic attack on polymer aromatic
rings by protons$^{[28]}$. Protons would preferentially attack the ortho and para ring
positions because the aliphatic polymer backbone would be an electron releasing
group for the aromatic rings. Most of the products detected by pyrolysis GC/MS
and TG-GC/MS can be derived from mechanisms beginning with ring protonation.
Thermal decomposition of ortho protonated aromatic rings in the polymer chain (G) can lead directly to the liberation of benzene, the primary catalytic cracking product, or may result in chain shortening.

Benzene cannot be obtained directly from para protonated aromatic rings in the polymer. However, para protonated rings can react with neighboring polymer chains to yield the same chain scission products that can be formed by ortho protonation.

The macrocation remaining after benzene evolution (H) may undergo chain shortening 6-scission to produce (I) and an unsaturated chain end, rearrange to form an internal double bond and protonate a neighboring aromatic ring (either by intra- or inter-molecular proton transfer), or cyclize to form an indane segment. The substantial quantities of indanes obtained by poly(styrene) catalytic cracking suggests that cyclization of (H) to form indane structures is a favored process.
consequence of chain unsaturation resulting from (H) might be the formation of conjugated polyene segments that may subsequently cyclize to form naphthalenes.

A minimum of three conjugated double bonds must be created in polymer chains before naphthalenes can be formed. As a result, naphthalene evolution during TG sample heating should be delayed relative to the evolution of alkyl benzenes and indanes, which can be formed from polymer segments without conjugated unsaturation. TG-GC/MS results revealed that the maximum rates of evolution of naphthalene and methyl naphthalenes from heated samples occurred at temperatures 15-20 °C higher than those at which the maximum evolution rates of alkyl
benzenes and indanes occurred, indicating that formation of naphthalenes was indeed delayed. This is illustrated by Figure IV.24, which shows the temperature dependent yields of benzene, methyl indane and naphthalene derived from TG-GC/MS analysis of the HPS/ZrO\textsubscript{2}/SO\textsubscript{4} sample.

Decomposition of (I), which might be formed from (G) or (H), can result in the formation of styrene or may lead to chain end unsaturation and neighboring ring protonation. Hydride abstraction by (I) would result in a saturated chain end. The lack of significant styrene production from any of the polymer/catalyst samples suggests that 6-scission of (I) to form styrene is not a dominant decomposition pathway at low temperatures. Chain end unsaturation derived from (I) may result in formation of indenes, which were detected in substantial amounts only when HZSM-5 catalyst was present. The restricted volume of the HZSM-5 channels apparently inhibited hydride abstraction pathways for (I), which resulted in increased production of indenes and styrene for the polymer/HZSM-5 samples compared to the other polymer/catalyst samples.
Figure IV.24 TG-GC/MS chromatographic peak areas as a function of sample temperature representing benzene, methyl indane and naphthalene derived from the HPS/ZrO₂/SO₄ sample.
Protonation of aromatic rings adjacent to methyl terminated chain ends (J) can result in the formation of alkyl benzenes, propene, and benzene, depending on how the macrocation decomposes.

Protonation of aromatic rings at styrene terminated chain ends (K) can also result in the formation of benzene and alkyl benzenes.
Macrocation (L), which can be formed from (G), (J), or (K), can undergo 6-scission to form styrene, rearrange to form a tertiary benzyl cation (M), or may abstract a hydride to form (J).
The tertiary benzyl cation (M), which would be preferentially formed by hydride abstractions in addition to rearrangement of (L), may be a precursor for chain unsaturation and for the formation of indenes.

If rearrangement of (M) results in chain unsaturation and intramolecular ring protonation, volatile indenes may ultimately result. If intermolecular ring protonation occurs, macrocation (G) would likely be formed.

Figure IV.19 shows that benzene can be obtained by poly(styrene) catalytic cracking at temperatures as low as 130 °C. The fact that the temperature at which volatile decomposition products were detected from polymer/catalyst samples was dependent on the catalyst acidity suggests that the rate limiting step in the acid
catalyzed decomposition of poly(styrene) was aromatic ring protonation. For all polymer/catalyst samples, benzene was the first volatile product detected when samples were heated in the thermogravimetric analyzer, which suggests that processes leading to benzene liberation were favored over those that resulted in the products detected at higher temperatures. This is consistent with the reaction schemes proposed here, which show that benzene can be easily formed from (G), but that formation of other volatile decomposition products is more difficult and may require macrocation rearrangement, hydride abstraction, or successive protonations. By examining the pyrolysis products of all polymer/catalyst samples, it can be seen that xylenes were only detected in polymer/HZSM-5 samples. This fact suggests that, due to the restricted HZSM-5 channel volume, methyl groups might readily transfer (e.g. from isopropyl benzene to benzene) leading to the formation of toluene and xylenes\textsuperscript{[44]}. Hansford et al reported that in the presence of acid catalysts, methyl group transfer from isopropyl benzene to benzene at temperatures above 500 °C can yield as much as 20% toluene and xylene\textsuperscript{[44]}. On the other hand, secondary reactions were minimized by rapid removal of primary volatile products from Si-Al/polymer and ZrO\textsubscript{2}/SO\textsubscript{4}/polymer mixtures.

Volatilization activation energies listed in Table IV.13 and species specific evolution profiles shown in Figures IV.18 to IV.23 indicate that the catalytic effect of each acid catalyst was greatest when they were in contact with the LPS polymer. This result suggests that the different end groups may have had an effect on the thermal stability of poly(styrene) polymers. The presence of butyl groups in the LPS
polymer may have contributed to the formation of butene and pentane when LPS/catalyst samples were pyrolyzed. However, the amounts of major cracking volatile products were not significantly affected by the different end groups. For example, product yields in Tables IV.16 to IV.21 show that benzene, which was the product obtained in the largest yield from catalytic cracking of polymer samples, was evolved in comparable amounts from polymer samples containing the same catalysts.

The large difference in molecular weights for the LPS and HPS polymers (2,700 amu vs 850,000 amu) might be expected to be an important factor in catalytic cracking processes. Successive cleavage of short polymer chains should more quickly lead to volatile products than cleavage of longer chains. However, low temperature benzene production does not require chain cleavage. Benzene evolution was always found to begin at a lower temperature for the LPS polymer than for the HPS polymer. Chain end aromatic rings should be somewhat more susceptible to electrophilic attack because electron release from the polymer backbone into these rings should be slightly greater than for the other aromatic rings in the polymer. Because the samples containing the LPS polymer had more chain ends than the HPS polymer, low temperature reaction rates for the LPS polymer would be consistently higher than for the HPS polymer, which would lead to the observed higher benzene evolution rates at low temperatures for samples containing the LPS polymer.
IV.5 Conclusions

Acid catalyzed poly(styrene) cracking involves many different parallel reactions and is quite complicated. The following general reaction scheme represents the primary reaction pathways. The initial step in poly(styrene) cracking is the protonation of polymer aromatic rings. Ortho protonation can readily lead to benzene evolution and the formation of a secondary macrocation, or may result in chain shortening, yielding a chain end cation and a saturated chain end. Cyclization of the secondary macrocation can lead to the formation of indane, methyl indane, and dimethyl indane. Hydride abstraction appears to be an important reaction pathway for chain end cations, except when the catalyst restricts the movement of polymer chains (e.g. HZSM-5). Saturated chain ends are the likely
source of alkyl benzenes, which can be formed after protonation of chain end aromatic rings. Rearrangements and 6-scissions of macrocations can lead to chain unsaturation, or, for chain end cations, the formation of unsaturated volatile products such as styrene and indenes. Conjugated polyene chain segments resulting from macrocation rearrangement can back bite to form naphthalenes.

The major volatile cracking products derived from LPS and HPS were different when catalysts were employed. Volatile product distributions were affected by the choice of catalyst as well as the cracking conditions. However, the relative yields of volatile cracking products were not significantly affected by the different end groups and molecular weights of the LPS and HPS polymers. Higher catalyst acidity caused polymers to be cracked at lower temperature. Therefore, product distributions and cracking temperatures for PS tertiary recycling methods can be modified by the choice of cracking catalyst.
IV.6 References


18. Y. Sekiguchi, T. Kuroki, Y. Furuhashi, M. Watanabe, T. Ikemura, N.


35. B.W. Wojciechowski, A. Corma, "Catalytic Cracking: Catalysts, Chemistry,


