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Thermal Degradation Of High Molecular Weight Polyethylene To Obtain Low Molecular Weight Polyethylene Wax

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THERMAL DEGRADATION OF HIGH MOLECULAR WEIGHT POLYETHYLENE TO OBTAIN LOW MOLECULAR WEIGHT POLYETHYLENE WAX

by

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ABSTRACT

The thermal degradation of high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) to low molecular weight waxes (Mw of ~700) were carried out to study the reaction kinetics of the degradation mechanism under various degradation conditions. The properties of the products produced under the various degradation conditions were also studied to understand the relationship between process and product properties. Thermal degradations were carried over a range of temperatures in two types of reactors, a resin kettle purged with nitrogen in which volatiles were allowed to distill-off, and under pressure in an unvented Parr reactor. These reactors were also operated with and without catalyst to understand the effect that catalyst may have on the degradation kinetics and product. Wax products generated under atmospheric conditions without catalyst had lower polydispersity but took longer to get to the final molecular weight. Catalyzed reactions under atmospheric conditions had higher polydispersity and produced lower molecular weight products that were easily distilled off as volatile liquids and gasses. Pressure reactions with catalyst produced the lowest molecular weight products, however polydispersity was high. Pressure reactions without catalysts produced waxy materials with the lowest polydispersity.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

List of Figures

List of Tables

Chapter 1   Introduction

Polyethylene waxes play an important part in the manufacturing of many goods in society today. They are used in a diverse range of applications from abrasive resistant inks, to rheology modifiers for hot melt adhesives, to coatings for fruit protection and preservation. Global demand for waxes reached an estimated 9.6 billion pounds in 2010 with petroleum based waxes comprising 85% of this total. Global wax demand is expected grow at rate of more than 2% from 2010 to 2020 [1]. In order to meet this demand, alternatives to the traditional polymerization of ethylene are being considered. One of these alternatives is the degradation of polyethylene waste into waxes with the desired molecular weight and distribution. Polyethylene wastes include both high density polyethylene (HDPE), traditionally used in plastic bottles, food containers and water pipes, and linear low density polyethylene (LLDPE) used in applications such as plastic bags and plastic wraps. It is estimated that 24% of all municipal waste in the United States is composed of plastics which include HDPE and LLDPE and of these materials only 8% are recovered through recycling [2].

Herein we study the thermal degradation of polyethylene through pyrolysis, so as to better understand the process conditions, kinetics and products that can be derived from this approach to wax production from waste polyethylene feed stocks. The final product is fragmented polyethylene similar in structure to the starting material but with lower molecular weight. This work centres on decreasing the chain length of the original polyethylene from approximately 3000 carbons to 50 carbons, which results in polyethylene waxes suitable for use in many applications.

The study of the thermal degradation of polymers, specifically polyethylene, has been ongoing for sixty years [3,4]. The products of polyethylene degradation generally include a liquid, a gas and a waxy residue. In many studies the waxy residue is alluded to and quantified for mass balance purposes, but it is rarely if ever characterized since wax production was not the purpose of those studies. The difficulty with which this solid residue can be solubilised for analysis may be a contribution factor for the lack of scientific data related to waxes produced from polyethylene degradation. As a result this difficulty some advanced characterization capabilities are required as for example high temperature GPC. High temperature GPC characterization has however been utilized in this work to shed light on these previously un-explored routes to wax production so as to quantify both the character of the products produced and the kinetics of the reactions

Chapter 2   Literature Review

The main differences between polyethylene wax, HDPE, and LLDPE is primarily molecular weight and degree of branching. Despite similar chemical formulas and structures, the difference in molecular weight results in different physical properties such as melting point, viscosity and hardness. HDPE and LLDPE typically have number average molecular weights from 20,000 to 100,000 g/mol while polyethylene waxes typically exhibit molecular weights in the 500 to 2000 g/mol range. There are several different species of materials that can be categorized as wax, however there are some characteristics that are common to most of them. They tend to melt above 45°C to give a low viscosity liquid, they tend to be insoluble in organic nonpolar solvents, and they are organic compounds which can be naturally occurring or not. Since the waxes used for this study are polyethylenes, these waxes will be saturated alkanes with the formula C_nH_{2n+2}. It has been proposed that high molecular weight HDPE and LLDPE can act as an alternative feedstock for producing polyethylene waxes by carrying out thermal degradation (pyrolysis) reactions [5,6]. In the past polyethylene has been typically degraded to the level of liquid hydrocarbon with fuels being the targeted product [7,8,9,10,11,12]. Those studies typically acknowledged the existence of a "waxy residue", but rarely characterized the composition or properties of it because it was regarded as a waste by-product. Pyrolysis is the thermal decomposition of organic material in the absence of oxygen whereby polymers can be broken down at high temperature yielding small fragments of similar composition to the original molecule. In this work pyrolysis of HDPE and LLDPE beyond their decomposition temperature at atmospheric pressure under a nitrogen purge in a resin kettle and in a sealed pressure

reactor were studied. The experiments in both cases were carried out with and without silica-alumina catalyst to see if either the temperature or the run time could be reduced.

2.1 Polyethylene

Polyethylene is a member of a class of materials known as polyolefins and is synthesized by the polymerization of ethylene monomer. It can have a wide range of molecular weights ranging from a few hundred to a few million grams per mole. The reaction equation below describes its synthesis in very general terms.
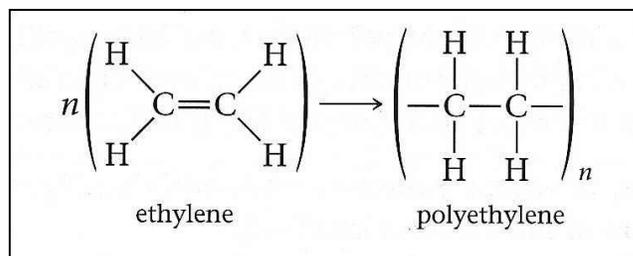
Figure 2.1 Synthesis of ethylene into polyethylene

Polyethylene is a versatile material and is the most common plastic in use today. This makes it an ideal target raw material for recycling and re-processing, not only to be remelted and recast as new polyethylene products, but also as a reactant in chemical reactions. The latter point is slightly counterintuitive due to the fact that polyethylene has traditionally been sought after for its chemical inertness. Despite its inherent chemical stability, it can and will undergo a free radical chain degradation reaction under the appropriate conditions. If polyethylene is targeted for recycling via thermal degradation, it is usually preferred if the resulting products have as little branching as possible and have as narrow a molecular weight distribution as possible. With this in mind it is

4

usually preferred to select high molecular weight polyethylenes with minimal branching such as for example LLDPE and HDPE.

2.1.1 Linear Low Density Polyethylene (LLDPE)

LLDPE contains a measurable amount of branching, however these branches are short and of low frequency so that it can be classified as "linear". These short branches prevent LLDPE chains from packing against one another so as to maintain a lower density than HDPE. LLDPE has a density of 0.924 g/cm^3 and a melting point of approximately 124°C. It is produced through a co-polymerization reaction of ethylene and longer chain olefins. As a result of the synthetic route used to manufacture it and its structure, it has a unique set of physical and rheological properties. These properties make it ideally suited for applications in plastic bags and plastic wraps.

2.1.2 High Density Polyethylene (HDPE)

HDPE differs from LLDPE in that it has little or no branching. As a result of the lack of branching the polymer chains can pack more tightly than in the case of LLDPE. Thus the resulting density of HDPE at 0.961 g/cm^3 is higher than that of LLDPE, as is the melting point (133°C). Although it is synthesized in much the same way as LLDPE, the branching can be controlled by selecting the right reaction conditions and also by the choice of catalyst. Like LLDPE, HDPE is produced using Ziegler-Natta catalysts

2.1.3 Polyethylene Waxes

Polyethylene waxes are petroleum based waxes that are short chain versions of the polyethylenes we are more familiar with (LLDPE, HDPE). They are referred to as petroleum based waxes because their backbone structure consists of carbon-carbon bonds, whereas naturally occurring waxes like plant and animal waxes have ester groups in their backbone (Figure 2.2). Short chain polyethylene waxes are synthesized in the same manner as their longer chain counterparts, via an ethylene polymerization with Zeigler-Natta catalyst.
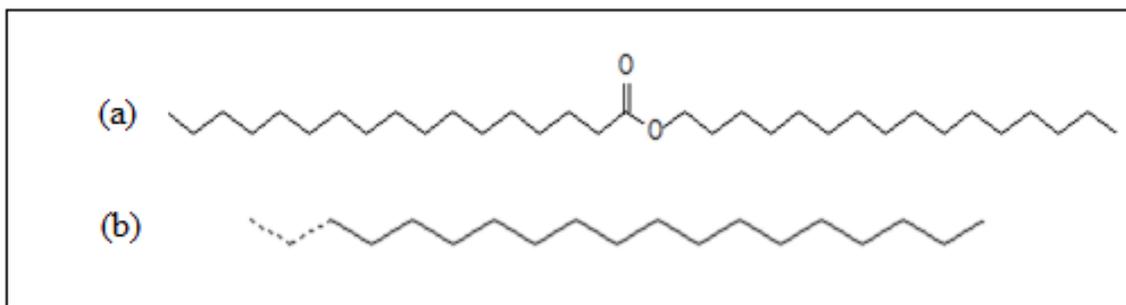
Figure 2.2 Structural difference between (a) a naturally occurring animal wax, and (b) synthetic polyethylene wax

2.2 Thermal Degradation of Polyethylene

Broadly defined, pyrolysis is a method of thermochemical degradation that occurs under an inert atmosphere. It is a special case of the more general process of thermolysis, which is simply the degradation of a polymer under atmospheric conditions in the presence of air. There have been many methods used to perform thermal degradation. Historically the most common method for performing thermal degradation of polyethylene was thermogravimetric analysis [13,14,15]. This method required using a small amount of polymer, usually 15 to 20 mg in a small platinum pan which hangs from

a spring. The oven is then heated to 500 to 1000°C and the kinetics were determined by correlating the decrease in weight to the volatiles collected. These experimental setups were not well suited to studying the degradation in molecular weight as a function of time since the temperatures were too high, the degradation kinetics too fast, and the sample size too small for GPC and other analysis of interest such as rheology, DSC and NMR. Reactor setups like the resin kettle and the Parr reactor used in this study overcome many of the deficiencies of a setup like TGA by allowing for the collection of a sufficient sample size to perform many of the analyses which were otherwise not possible with TGA. These setups also allow for lower run temperatures presumably because the heat transfer is better as a result of adequate mixing [7]. Several other setups have been used to perform polymer degradation such as fluidized bed [13], spouted bed reactors [16], and some specially designed reactors utilizing reactors immersed in molten salt baths [17]. Murata et al. have studied degradation in a continuous flow reactor at about 1.5 kg/hr [18]. A general scheme for the mechanisms and products of polymer degradation is given in Figure 2.3

2.3   Thermal Degradation by Free Radical Chain Theory

The degradation of polyethylene progresses via a radical chain reaction mechanism which is similar to the mechanisms derived by Flory for polymerization of polyolefins [19]. All reactions that proceed by radical chain mechanisms share a common set of steps whether they be a reaction in which a polymer is synthesized from monomers or a reverse acting degradation process in which a polymer molecule is broken

down into smaller polymer fragments or monomers. These three common steps are initiation, propagation and termination.

2.3.1 Initiation

It has been reported as early as 1949 that polyethylene begins to undergo the early stages of degradation at approximately 360°C [3]. When polyethylenes are heated to this temperature they will begin undergo thermal degradation which is a chain reaction mechanism, similar in nature to that of a polymerization reaction as seen in Figure 2.4. This reaction may commence in one of two ways. The polymer molecule can break at random points along its main carbon chain which is known as random chain scission (Equation 2.1) or it can sequentially break end units off the main chain, which is known as end chain scission (Equation 2.2). Polyethylene has been specifically determined to undergo random scission as opposed to end chain scission [4, 5]. The main reasoning for this is that polymers that undergo end chain scission generate high amounts of monomer as is the case when polystyrene or polymethylmethacrylate undergo degradation.
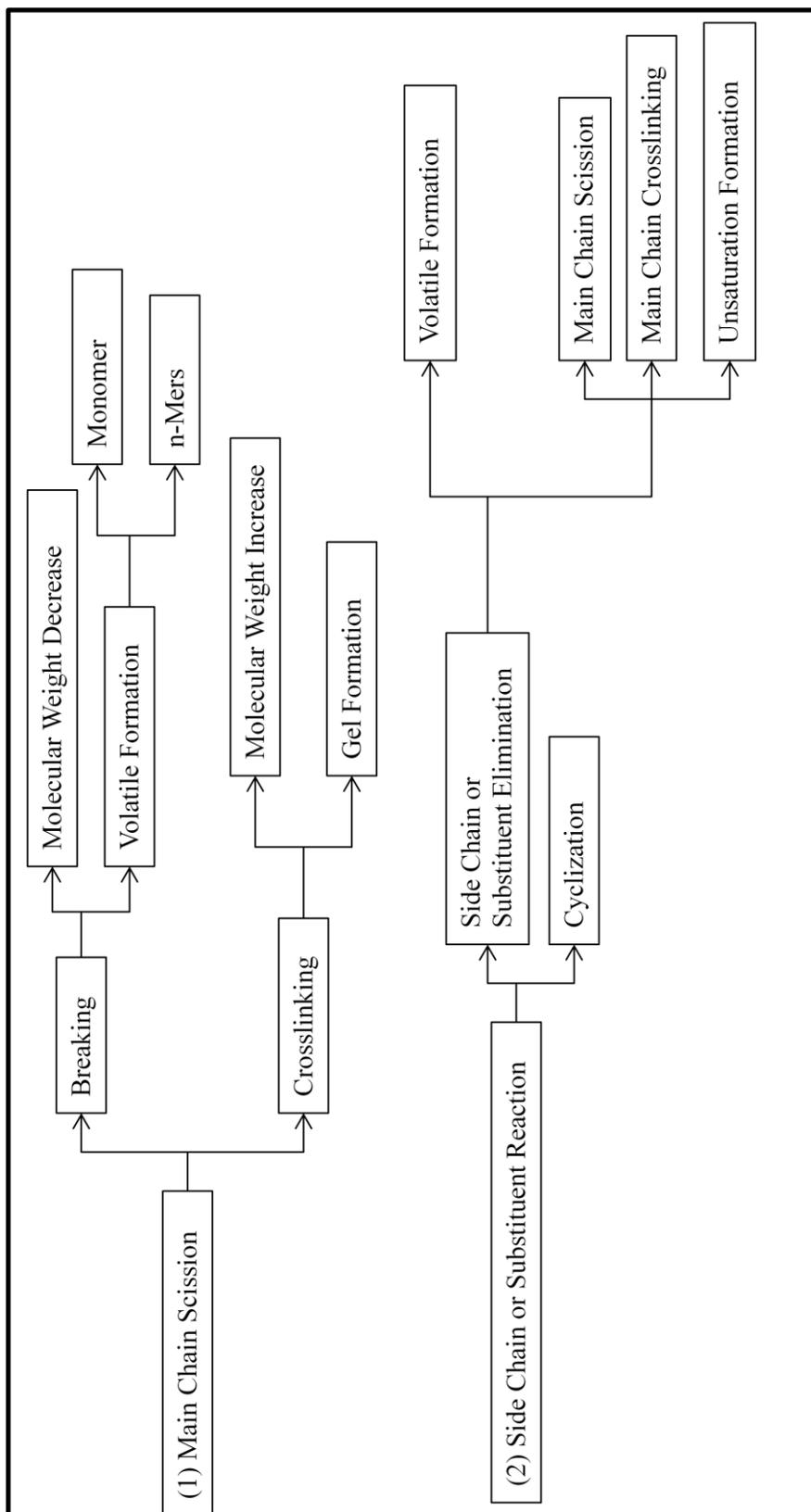
Figure 2.3 Simplified scheme for polymer degradation [20]

2.3.2 Propagation

Once the chain reaction has been initiated, the reaction continues through the propagation of free radicals. Polyethylene can undergo one of three reactions, the first of which is depropagation (Equation 2.3). Depropagation is effectively an unzipping of the polymer molecule where monomer units are removed from the end of the polymer chain. As mentioned previously this is not believed to be the main reaction pathway because of the low amount of monomer that evolves during polyethylene degradation. This leaves intramolecular and intermolecular hydrogen transfer as the main methods for propagating the reaction.

Intramolecular hydrogen transfer (Equation 2.4) is a process whereby a radical molecule takes a hydrogen atom from a location on its own polymer chain cleaving the molecule thus producing two new molecules. The first is a shorter polymer chain with a double bond between the carbon atoms from which it abstracted a hydrogen atom and the second is a new radical species that consisting of the other portion of the cleaved molecule.

Intermolecular hydrogen transfer (Equation 2.5) is an identical process, however it occurs between two different molecules. A radical molecule will take a hydrogen atom from another molecule to pair up with its lone electron. In the process it cleaves the molecule from which it abstracted a hydrogen atom to create a new polymer molecule and a radical. These transfer reactions will continue until the radical population is terminated.

2.3.3 Termination

Radical termination can occur via a number of pathways, although not all of them are equally preferred. In the case of polyethylene disproportionation is considered to be most common mechanism for the termination of radical. In this step two radicals come together to form an alkane and an olefin as shown in Equation 2.7 [21]. Coupling reactions are not the preferred route to terminate radical reactions because the process is highly exothermic and must dissipate the energy. At elevated temperatures this is difficult to do [22].

2.4 Catalytic Degradation

There has been much work done in the area of catalyzed thermal degradation of polyethylenes [23,24,25,26,27]. Most thermal degradation reactions of polyethylene utilize catalysts in an attempt to lower the temperature or increase the rate of reaction [28,29]. In most cases zeolites or amorphous silica-alumina catalyst have been found to be the most effective for the thermal degradation of polyethylene [30,31,32,33,34]. It has been shown that the use of catalysts, in particular amorphous silica-alumina, during thermal degradation of polyethylene significantly reduced the apparent activation energy as compared with uncatalyzed thermal processes [20]. Catalysts have been reported to increase the yield of gas and liquid products as compared to reactions without catalyst [7].

Initiation

$$P_n \rightarrow R_r^\bullet + R_{n+r}^\bullet \qquad\qquad (2.1) \quad \text{(random-chain scission)}$$

$$P_n \rightarrow R_n^\bullet + R_E^\bullet \qquad\qquad (2.2) \quad \text{(end-chain scission)}$$

Propagation

$$R_n^\bullet \rightarrow R_{n-1}^\bullet + P_1 \qquad\qquad (2.3) \quad \text{(depropagation / unzipping)}$$

$$R_n^\bullet \rightarrow R_{n-m}^\bullet + P_m \qquad\qquad (2.4) \quad \text{(intramolecular H transfer/random scission)}$$

$$P_m + R_n^\bullet \rightarrow P_{m-j} + P_n + R_j^\bullet \qquad\qquad (2.5) \quad \text{(intermolecular H transfer)}$$

Termination

$$R_m^\bullet \rightarrow P_m \qquad\qquad (2.6) \quad \text{(first order coupling)}$$

$$R_m^\bullet + R_n^\bullet \rightarrow P_{m+n} \qquad\qquad (2.7) \quad \text{(second order coupling)}$$
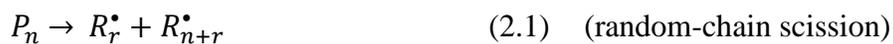
$$R_n^\bullet + R_m^\bullet \rightarrow P_m + P_n \qquad\qquad (2.8) \quad \text{(disproportionation)}$$

Figure 2.4 Generalized reaction mechanism describing steps for thermal degradation of polymers[20].

2.5   Objectives

Whereas previous work in the field of thermal degradation of polyethylene has focused on the liquid products of degradation, the work presented herein will focus on the solid products of degradation using batch type reactor setups. The specific objectives of this study are as follows:

1) To determine a set of operating conditions including process setup which will convert a high molecular weight polyethylene HDPE and LLDPE into a low molecular weight polyethylene wax.

2) To study and measure the degradation kinetics of HDPE and LLDPE polymer melts by continuous sampling during a degradation reaction. The parameters to be varied between experiments include reactor setup, time, temperature, pressure and the presence or absence of catalyst.

3) To characterize the solid products obtained from pyrolysis and compare them to polyethylene waxes so as to determine if thermal degradation provides an adequate route to wax production. Characterization techniques include molecular weight determination by high temperature gel permeation chromatography (GPC), rheological analysis, melting point analysis by differential scanning calorimetry (DSC), and high temperature nuclear magnetic resonance spectroscopy (NMR).

Chapter 3   Experimental Setup and Procedure

3.1   Equipment

Two approaches to polyethylene degradation were studied. The first degraded the polyethylene under atmospheric pressure and nitrogen blanket and the second degraded polyethylene in a sealed pressure vessel where volatiles were not allowed to escape. The equipment used for experiments at atmospheric pressure was selected so that samples could be taken during an experiment and a profile of the degradation over time could be established. The equipment used for the experiments conducted under pressure did not permit sampling.

3.1.1   Degradation at Atmospheric Pressure under Nitrogen Atmosphere

For experiments carried out under atmospheric pressure, the main vessel was a 500 ml glass resin kettle. The lid and the kettle were sealed with vacuum grease and a three spring clamp. The resin kettle was heated by a 270 W Glas-Col heating mantle model 100B-TM570. Four ports were situated on the lid of the resin kettle; one in the centre of the lid and three equally spaced around the perimeter of the lid. The centrally located port was for the stainless steel agitator shaft which was fitted with two metal P4 impellers that were 5 cm in diameter; one to mix the polyethylene melt and one to mix the reactor headspace to ensure that the inert purge gas was well mixed. The agitator shaft was driven by an IKA RW20 DZM mixer. The other three ports were used for a nitrogen purge, a Type K thermocouple which was connected to the temperature controller as part of a feedback control loop, and the final port was used to allow volatiles

14

to escape to the distillate receiver. A rotatmeter was also used to adjust the flow of nitrogen into the resin kettle to inert the headspace of the reactor, which under normal running conditions had flammable volatile gases present. A Digisense model 89000 temperature controller with built in PID control and auto tune was used to control the reaction temperature via the thermocouple inserted inside the resin kettle. The distillate receiver, which was a three necked round bottom flask, was connected to the resin kettle with standard glass fittings having 24/40 ground glass connections. Cooling of the glass three neck round bottom receiver was accomplished by submerging it in dry ice pellets with a temperature of -78°C. The receiver in turn was connected to a nitrogen bubbler filled with mineral oil. The bubbler served to provide a slight back pressure so that the entire setup was flooded with nitrogen while simultaneously allowing it to be vented to the atmosphere. The setup is shown in Figure 3.1.
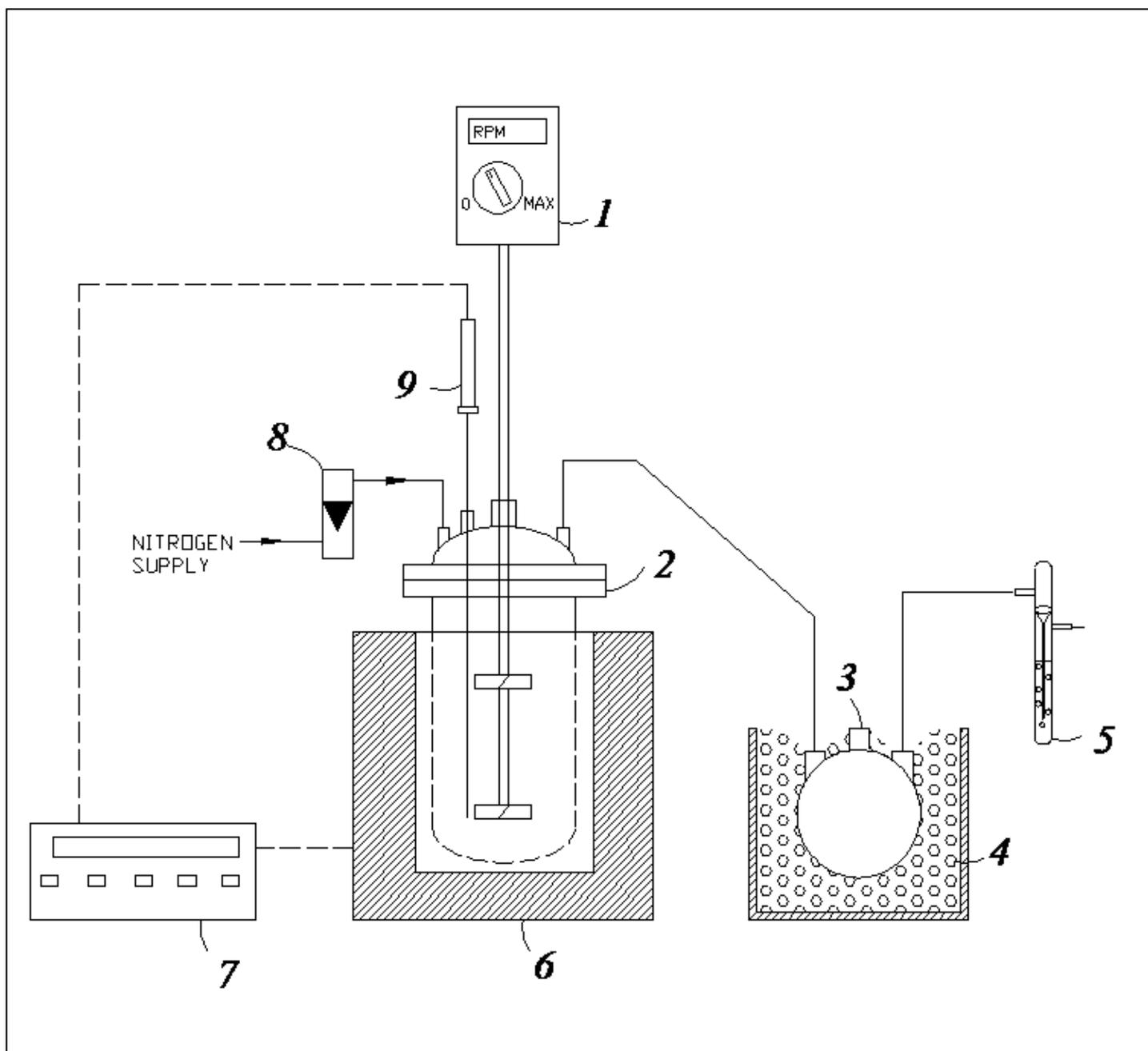
Figure 3.1 Configuration of resin kettle for degradation reactions at atmospheric pressure,1: IKA RW20 DZM mixer; 2: 500 ml glass resin kettle; 3: 3-neck round bottom flask (middle neck plugged); 4: Dry ice; 5: Mineral oil bubbler; 6: Glas-Col heating mantle; 7: Digisense model 89000 temperature controller; 8: Rotameter to adjust nitrogen purge; 9: Type K thermocouple.

3.1.2   Parr Pressure Reactor

For experiments carried out in a sealed vessel, a Parr Pressure Reactor model 452HC was used. The reactor had a 300 mL capacity with a maximum allowable working pressure of 2000 psi. The reactor utilized a magnetic drive so that the impeller shaft was completely sealed within the reactor. The sealed shaft allowed for the separation of process and environment and for an accurate pressure measurement to be made without any leakage to the environment. Agitation is accomplished by a single impeller 4 cm in diameter attached to the impeller shaft. There are 5 ports on the lid of the reactor of which four are utilized and one is capped. Temperature was controlled by a Digisense temperature controller model 89000. A type K thermocouple and the Glas-Col heating mantle were both attached to the Digisense controller. The controller would increase or decrease power to the aluminum housed mantle based on the difference between the setpoint and the actual temperature. A Parr 4840 controller is used to control the electrically driven agitator. There are two ball valves on the top of the reactor that are used to vent any built up pressure when the reaction is complete. There is a 0.25 inch inconnel rupture disc designed to fail at 2000 psi. The setup is shown in Figure 3.2.
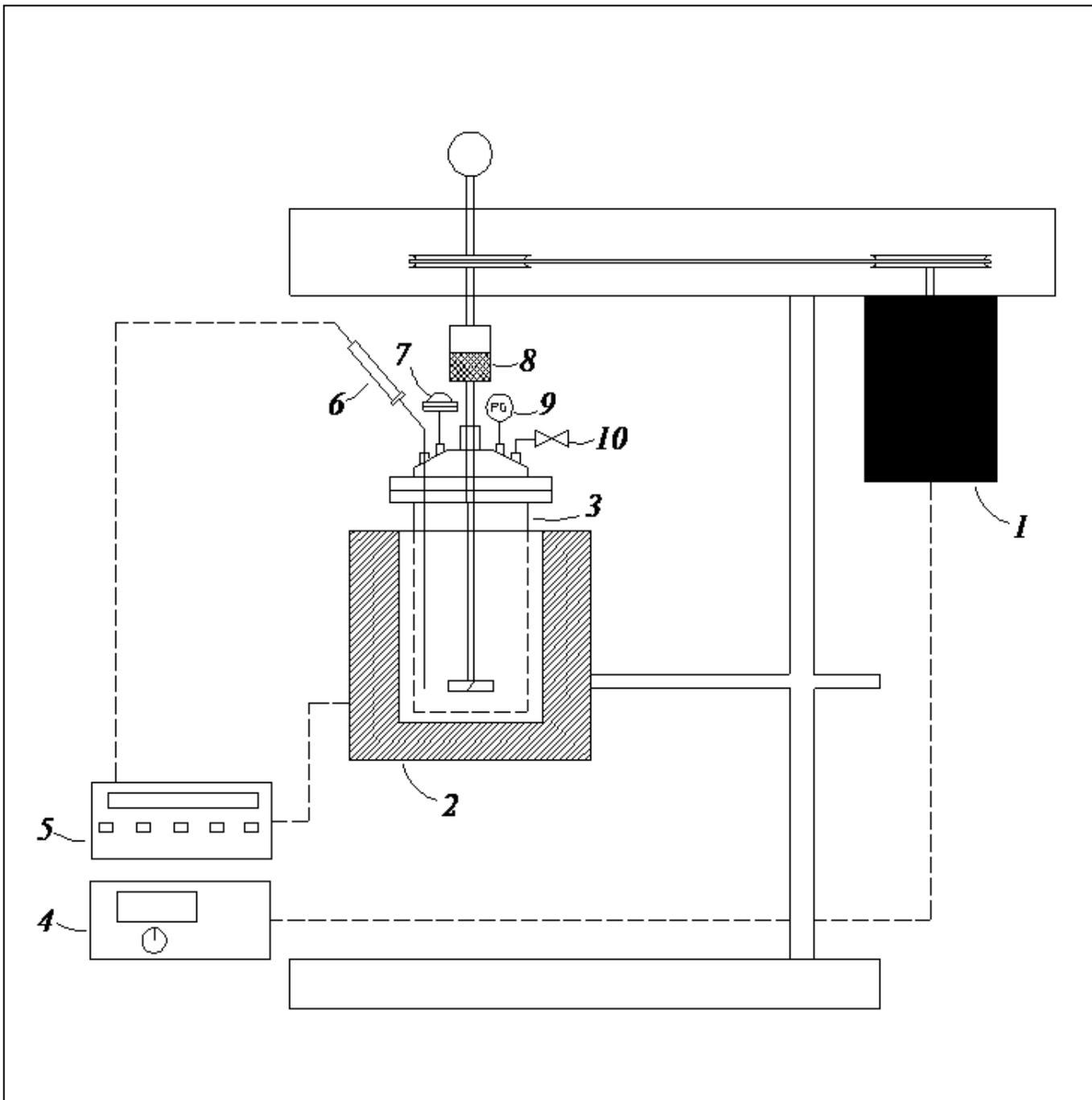
Figure 3.2 Configuration of Parr reactor for degradation under pressure, 1: Electric motor connected by belt to mixer assembly; 2: Adjustable height Glas-Col heating mantle; 3: 300 ml Parr reactor ; 4: Parr 4842 RPM controller; 5: Digisense model 89000 temperature controller; 6: Type K thermocouple; 7: 2000 psi rupture disc; 8: Magnetic coupling ; 9: Pressure gauge; 10: Vent valve.

3.2   Materials

The degradation experiments conducted in this study utilized LLDPE and HDPE sourced from Nova Chemical. Both materials were supplied in pellet form from the manufacturer. The linear low density polyethylene used was Novapol PI-2024-A. It had a number average molecular weight of 14,331 g/mol and a polydispersity of 3.40. The high density polyethylene used was SCLAIR-2908. It had a number average molecular weight of 18,734 g/mol and a polydispersity of 3.08. Table 3.1 outlines of the physical properties of interest and their associated units with regards to each of the polyethylenes selected for this study. Each of the properties listed in Table 3.1 is measured using a standardized test method as determined by the American Society for Testing and Materials (ASTM). The standardized methods allow different materials to be accurately compared. Table 3.2 lists the various molecular weights of interest as well as the polydispersity of the materials used in this study. The molecular weight of these materials was determined by high temperature gel-permeation chromatography utilizing the method outlined in Section 3.4.1 below. Throughout the duration of this work when referring to molecular weight, the number average molecular weight will be referred to. For experiments where the effect of catalyst on the degradation of polyethylene was examined, a Silica-Alumina catalyst Grade 135 from Aldrich was used. Silica-Alumina is a synthetic substance that can be used as both a catalyst and a catalyst support. The experiments conducted in this study utilize it directly, without modification, as catalyst. It was selected based on its low cost and prevalent use in hydrocarbon cracking, a closely related field to this body of work.

Table 3.1 Physical Properties of Materials Used in Experiments

Physical Properties	ASTM	Units	NOVAPOL PI-2024-A	SCLAIR 2908
			LLDPE	HDPE
Melt Index(3)	D 1238	g/10 min	20	7
Density	D 792	g/cm3	0.924	0.961
Tensile Strength @Yield	D 638	MPa (psi)	13 (1,900)	29 (4,200)
Elongation @ Break	D 638	%	200	1,200
Flexural Modulus	D 790	MPa (psi)	415 (60,200)	1,280 (185,000)
Hardness, Shore D	D 2240	n/a	55	65
Softening Point (Vicat)	D 1525	°C (°F)	91 (196)	129 (264)

Table 3.2 Molecular Weight of Materials Used in Experiments

Molecular Weight	NOVAPOL PI-2024-A	SCLAIR 2908
	LLDPE	HDPE
Mp	41,093	42,427
Mn	14,331	18,734
Mw	48,796	57,695
PDI=Mw/Mn	3.4	3.08

3.3 Methods

3.3.1 Thermal Degradation Using Glass Resin Kettle

For experiments carried out in the glass resin kettle, 200 g of polyethylene was weighed out and put into the reactor. After charging the polyethylene to the reactor the rest of the components were assembled as shown in Figure 3.1. The setup was vented to atmosphere through a mineral oil bubbler. Nitrogen was purged through the reactor at a rate of 0.5 standard cubic feet per hour (scfh) in order to inert the atmosphere and prevent ignition of flammable hydrocarbon vapors being emitted during the experiment. Once the reactor was fully assembled and the nitrogen purge was on, heating was commenced. The mixing could not be started until the temperature reached approximately 300°C for LLDPE and 350°C for HDPE because below these temperatures the viscosity of the material was too high for the mixer. The rotational speed of the impeller was set at 150 rpm for all experiments. The RPM was determined qualitatively by observing the movement of the polymer melt to ensure there was adequate mixing with no dead zones at all the operating temperatures. The time to reach the running temperatures, which were between 380°C and 415°C, was approximately one hour. After reaching the running temperature the reaction was allowed to proceed for a pre-determined amount of time. For experiments performed without catalyst, the reaction was allowed to proceed for 210 minutes. In experiments that utilized catalyst, the catalyst was charged to the reactor along with the initial charge of polyethylene and these experiments were run for 120 minutes. The amount of catalyst used was 5% of the weight of polyethylene, so for all runs in the resin kettle that used catalyst, 10 g of Si-Al catalyst was charged with 200

21

g of polyethylene. Experiments with catalyst were only allowed to proceed for 120 minutes due to the rapid rate of degradation at temperatures in excess of 400°C. When running at 415°C with catalyst, a large portion of the reactor load volatilized after 60 minutes.

After the material had reached the predetermined running temperature for that experiment, which took approximately 60 minutes, samples were taken at regular intervals removing a barbed glass fitting through which nitrogen was being purged into the reactor. The sample was scooped out with a metal spatula.

For experiments that did not use catalyst, sampling was performed every 30 minutes over the course of the 210 minute run. Because the catalyst experiments only lasted for 120 minutes, sampling every 30 minutes after the experiment reached the temperature setpoint would have only provided two data points. Therefore the sampling frequency was increased so that more data points could be obtained to develop a curve comparable to the 210 minute run. As a result sampling was therefore performed every ten minutes during runs with catalyst.

3.3.2   Thermal Degradation in a Parr Reactor

For each of the experiments using the Parr reactor a total of 100 g of polyethylene was used. For experiments where Si-Al catalyst was used, the catalyst loading was 5% which was similar to the low pressure experiments. For pressure runs this resulted in 5 g of catalyst being used. The materials were loaded into the reactor and then the reactor was sealed, at which point heating commenced. In a similar fashion to the low pressure

reactions, the mixing could not be started until the temperatures reached approximately 300°C and 350°C for LLDPE and HDPE respectively. Reactions in the Parr reactor were run at an impeller speed of 188 rpm. The difference in speed between the Parr and the resin kettle was an attempt to keep the impeller tip speed the same in both setups. Equation 3.1 was used to ensure equal tip speed.

$$Tip\ speed = \pi DR \qquad (3.1)$$

where D and R are the diameter and rotational speed of the agitator. When the temperature setpoint was reached the reaction was allowed to proceed for a predetermined amount of time. The pressure before heating was commenced was atmospheric pressure, and as the degradation proceeded at the temperature setpoint, the pressure inside the reactor began to climb as volatile materials were generated but not allowed to escape. At the end of the reaction the Parr reactor was cooled down by placing it in a container of dry ice, while still allowing it to be stirred. The material was then removed from the vessel as degraded polyethylene product. After cooling the reactor to room temperature the pressure did not return to 0 psig, rather there was approximately 5 psig of pressure remaining in the reactor. This was due to the evolution of gaseous volatiles which were not condensable at room temperature (~25°C). When the reactor was vented the total loss due to the release of the uncondensable gases amounted to approximately 3 g of the original 100 g charge, giving a batch yield of 97 g.

3.3.3 Control Tuning

Both sets of reactions utilized a Digisense model 89000 temperature controller. This particular temperature controller had PID control in which the control parameters could be automatically determined using a feature called Auto-tune. The Auto-tune feature was selected at the very beginning of the experiment prior to commencing heating. By the time the temperature had reached the setpoint for the experiment, the controller was able to determine the characteristics of the system and come up with values for proportional band, integral time and derivative time. Our experiments were conducted with $P = 43$, $I = 402$ sec and $D = 96$ sec.

3.4 Analytical Methods

The primary analytical method used to characterize the degradation products was high temperature gel-permeation chromatography (HT-GPC). This method was used to determine the molecular weight of the materials. Another important analysis was carbon-nuclear magnetic resonance spectroscopy (C-NMR), which was used to determine the structure of the materials being generated. Other analytical techniques employed shed light on the physical characteristics of the reaction products. These methods included differential scanning calorimetry (DSC) which measured melting point, as well as rheological properties which were determined with the use of a rheometer.

3.4.1 Gel-Permeation Chromatography (GPC)

High temperature gel-permeation chromatography (HT-GPC) was used to determine the molecular weight distributions of the products developed from the degradation reactions. The standard test method ASTM D6474-99 entitled "Standard Test Method for Determining Molecular Weight Distribution and Molecular Weight Averages of Polyolefins by High Temperature Gel Permeation Chromatography" was used to prepare and measure the samples. The samples were separated on a two Polymer Labs 5μm Mixed-D columns which are linear between molecular weights of 200 to 400,000. The columns were calibrated using polystyrene standards from a molecular weight of 580 to 280,500 g/mol. The results relative to polystyrene standards were then converted to actual polyethylene molecular weights using the Mark-Houwink parameters for polystyrene and polyethylene. The samples were analyzed on a Polymer Labs 220HT system using refractive index detection using a mobile phase of 1,2,4-trichlorobenzene (TCB). The entire system was heated to 140°C. The samples were prepared at a concentration of approximately 4 mg/mL TCB at 140°C. Injection size was 100 μL. The following Mark-Houwink constants were used to convert MW's from polystyrene reference results to polyethylene actual molecular weights and were obtained from the standard test method:

$$\text{Polystyrene } K_{(PS)} = 1.9 * 10^{-5} \text{ L/g} \qquad \alpha = 0.655 \qquad\qquad (3.2)$$

$$\text{Polyethylene } K_{(PE)} = 3.9 * 10^{-5} \text{ L/g} \qquad \alpha = 0.725 \qquad\qquad (3.3)$$

$$K_1 M_{1PS}^{\alpha+1} = K_2 M_{2PE}^{\alpha+1} \qquad\qquad (3.4)$$

3.4.2 Carbon-Nuclear Magnetic Resonance Spectroscopy (^{13}C-NMR)

The ^{13}C-NMR was used to obtain the structure of the degradation products. In particular this analysis was used to test for the branching of the products. The goal was to start with both HDPE and LLDPE, which are branched, and make a final product that was both short chain and linear. Approximately 100 mg of the wax sample were dissolved in 550 μL deuterated benzene and ^{13}C-NMR spectra were obtained using a Bruker Avance 400 NMR spectrometer at 75°C. Several samples were found to be insufficiently soluble at those conditions and experiments for those samples were repeated using deuterated toluene at 105°C yielding acceptable solubility. Using inversely-gated pulse sequence and 5 s repletion time enables quantitave conditions for the similar carbons (at least for the methylenes).

3.4.3 Differential Scanning Calorimetry (DSC)

Analysis of product melting point was performed by a TA Instruments DSC Q-1000. Products of degradation with a narrow melting range would indicate a narrow molecular weight distribution and vice-versa. For these measurements approximately 5 - 10 mg of sample was weighed out into a hermetic pan and placed inside the instrument auto sampler. A pre-programmed heating method was used to establish the melting point. The instrument equilibrated at -50°C followed by a ramp at 10°C/min to 150°C. From 150°C the temperature was ramped down at -10°C/min to 50°C. Finally a second ramp at 10°C/min back up to 150°C was performed.

3.4.4 Rheological Measurements

The viscosity of the reaction products was analyzed by an Ares G2 rheometer using a parallel plate attachment. The viscosity of the material is of interest due to the fact that the products of degradation should show low viscosity up to the melt/freeze point, at which time the viscosity should increase rapidly. This property of the wax is important to its various applications and again relates to the molecular weight distribution of the wax produced. The Ares G2 is a controlled strain rheometer in which a stress is applied by the bottom plate and the resultant strain is measured by the top plate. Approximately 5-10 mg of sample was loaded onto the bottom plate which was heated to 140°C. When the sample was molten, the top plate was set to a gap of 500 μm and the excess was wiped away. The rheometer then executed a program in which the temperature was decreased at 2°C/min to a final temperature of 40°C. The viscosity at each temperature was measured and a profile of the viscosity over the temperature range was obtained.

Chapter 4   Results and Discussion

The objective of performing degradation experiments in the sealed Parr Reactor was to examine the effect of pressure on the rate of degradation, and also to see the effect of not allowing any of the volatile components to constantly escape as the reaction progressed. Likewise the primary objective of carrying out the degradation experiments in the glass resin kettle was to measure reaction kinetics at low pressures and under nitrogen atmosphere and to characterize the materials produced by this process in contrast to the kinetics and product properties produced by the high pressure reactor process. It is presumed that the presence (high pressure) or absence (atmospheric pressure) of low molecular weight species will affect the degradation rate of the polyethylene and the residual material properties. For example, short chain volatile materials exiting the low pressure reactors might carry with them radical species that affect the degradation rate. Thus slower degradation rates might be expected in the reactions carried on at atmospheric pressure since a lower radical population may exist. Similarly, this differentiated radical population may lead to differences in the termination kinetics and thus the degree of branching of the final product.

The process of thermal degradation generally leads to three categories of products; a non-condensable gaseous component, liquid distillates and solid residues. Whereas almost all of the previous work in the area focused on the production of liquid hydrocarbons, the work presented here focuses on the products of degradation which are solid at room temperature. As such, the majority of the analyses performed herein focus on the solid products of degradation. This presents a unique challenge due to the fact that the solid products are generally insoluble in most solvents at room temperature. As a

result, advanced characterization techniques are required such as high temperature GPC and variable temperature NMR are required.

The figures that follow show two styles of plots. The first is a line graph showing the molecular weight and polydispersity versus time. The primary purpose of these figures is to show how the molecular weight and the molecular weight distribution of the polymer melt changes with time. This data represents a weighted average of the populations shown in a second style of plots, which are included here because they convey a great deal of additional information. In examining the chromatograms we can see precisely how the molecular weight distribution is changing over the course of the experiment. By relying only on the line graphs one could erroneously conclude that the material is simply a normal distribution of molecular weights that is both getting smaller and growing wider as time progresses. Only by examining the chromatograms can we see precisely what is happening to the material in the reactor over course of the experiment with not only unimodal but bimodal distributions evolving over time.

In the resin kettle setup, there is a 60 minute gap from the time at which heating is commenced until the first sample is taken. This represents the time to heat the reactor from room temperature to the setpoint for the experiment. The first data point at 0 minutes on the molecular weight versus time graphs (ie. Figure 4.1) was the molecular weight of the starting material which was measured beforehand. The second data point, at 60 minutes, was taken when the reactor had reached the setpoint for the reaction. In the Parr reactor setup there was no sampling, but like the resin kettle the first data point at 0 minutes was the previously measured molecular weight of the starting material (ie. Figure 4.7). The next data point at 120 minutes represents a 60 minute heat up time plus

60 minutes of degradation at the setpoint before being cooled to room temperature with dry ice.

The use of a sealed versus unsealed reactor led to a major difference in the way the data was collected for studying reaction kinetics. For the resin kettle samples were taken over the course of an experiment to build the molecular weight versus time profile. This of course was impossible to do with the Parr reactor due to the fact that the contents were under pressure. Therefore, for the Parr reactor only one data point could be obtained per experiment since the material could only be sampled after the reaction was allowed to proceed for its predetermined time. At the conclusion of the reaction, the aluminum housed heating mantle, which had adjustable height, was lowered away from the Parr reactor while a bracket held the Parr reactor in place. A small container was lifted in place of the heating mantle so that the reactor sat in the bottom of the container while still being attached to the mixer. Finally the container was filled with dry ice effectively covering the outer surface of the Parr reactor and cooling it.

4.1   Experiments Performed

Table 4.1 is a comprehensive list of all the experiments performed in this study. The experiment list is the result of varying five different factors at two different levels (2^5) resulting in a total of 32 different run conditions. When repeats were added for reproducibility, the number of experiments increased significantly. The five factors investigated included reactor setup, polyethylene type, presence of catalyst, time, and run temperature. The reactor setups were Parr and resin kettle, the polyethylene type was

Table 4.1 Reactor setup and experimental conditions used in this study

Setup	Conditions					
	Temperature	Pressure	Materials	Catalyst	Experiments	Samples
Resin Kettle Temperature	380°C	Atmospheric	LLDPE	NO	3	0,60,90,120,150,180,210 min
			HDPE		3	0,60,90,120,150,180,210 min
	415°C	Atmospheric	LLDPE	NO	3	0,60,90,120,150,180,210 min
			HDPE		3	0,60,90,120,150,180,210 min
Resin Kettle Temperature + Catalyst	380°C	Atmospheric	LLDPE	5% SiAl	3	0,60,70,80,90,100,110,120 min
			HDPE		3	0,60,70,80,90,100,110,120 min
	390°C	Atmospheric	LLDPE	5% SiAl	3	0,60,70,80,90,100,110,120 min
			HDPE		3	0,60,70,80,90,100,110,120 min
Parr Reactor Temperature + Pressure	380°C	Pressure	LLDPE	NO	2	120,180,300 min
			HDPE		2	120,180,300 min
	415°C	Pressure	LLDPE	NO	2	120,180,300 min
			HDPE		2	120,180,300 min
Parr Reactor Temperature + Pressure + Catalyst (No repeats)	380°C	Pressure	LLDPE	5% SiAl	1	120,150,180 min
			HDPE		1	120,150,180 min
	415°C	Pressure	LLDPE	5% SiAl	1	120,150,180 min
			HDPE		1	120,150,180 min

LLDPE and HDPE, the catalyst was either present or not, the time was long (210 min in resin kettle and 300 min in Parr) and short (120 min in resin kettle and 180 min in the Parr) and the temperature levels were 380°C and 415°C, except for reactions in the resin kettle involving catalyst which were carried out at 380°C and 390°C. Also, for degradation involving catalyst the reaction time had been reduced to a maximum of 120 minutes from 210 minutes.

4.2   Thermal Degradation of LLDPE

The thermal degradation of LLDPE under atmospheric conditions in a resin kettle was carried out at 380°C and 415°C. The reaction temperatures selected were based on a twofold approach. Firstly, a set of preliminary temperatures was determined by reviewing the literature regarding previous work in similar reactor configurations. Secondly, these temperatures were then used to perform screening experiments to determine optimal running temperatures. An attempt was made to select running temperatures that would bracket both a low and high level of degradation in our different experimental setups for producing waxy materials. Due to the fact that the materials characterization had a long turnaround time compared to the experimental time, running parameters were originally chosen based on physical characteristics of products such melting point and rheological measurements. The conclusion was that below 380°C there was very little degradation occurring while above 415°C most of the materials would be degraded to liquid or volatiles in a short time. Other adjustments were made to the operating conditions when running experiments using catalysts. During the screening runs with catalyst in the resin kettle, a temperature of 415°C for 210 minutes caused all of

the material to be degraded and distilled off from the reactor. In order to address these faster kinetics with catalyst and ensure the production of waxy material, the temperature was lowered to 390°C which still left only a small amount of waxy residue in the resin kettle at the end of the reactions. In addition to lowering the temperature, the reaction time was also reduced so as to ensure that a maximum of the desired waxy product was produced. Thus with catalysts in the resin kettle, reactions were stopped after a period of 120 minutes after heating was commenced.

The thermal degradation experiments in the Parr reactor were also carried out at temperatures of 380°C and 415°C. The temperatures did not have to be altered to control the distillation of volatiles since the reactor was sealed. This closed system provided other challenges in that the evolution of volatiles still occurred which resulted in a build-up of pressure in the reactor. As a result, during experiments in the Parr reactor where catalyst was used, experiments had to be shortened so as not to approach or exceed the maximum operating pressure of the reactor which was 2000 psi. Thus experiments with catalyst and under pressure typically lasted 180 minutes from the time heating commenced.

4.2.1 Degradation of LLDPE Under Atmospheric Pressure in a Using Resin Kettle

Figure 4.1 shows the number average molecular weight and polydispersity of LLDPE versus time at 380°C and 415°C. When examining Figure 4.1 it is evident that the molecular weight decreases rapidly in the first 90 minute of the reaction, however the rate of degradation decreases considerably over the next 120 minutes. A likely

explanation for this decrease is that early on random breaks in the carbon backbone of the molecule will result in fragments that can be significantly smaller than the parent molecule from which they broke off. As the molecular weight of the polymer melt in the resin kettle decreases, the length of the carbon chain and subsequently the number of potential sites for random scission also decreases. As time progresses the resulting fragments that result from a random break in the carbon chain are unlikely to be significantly smaller than the parent molecule from which they broke off. This results in a decrease in the rate of molecular weight reduction and a flattening of the curve on the molecular weight versus time graph.
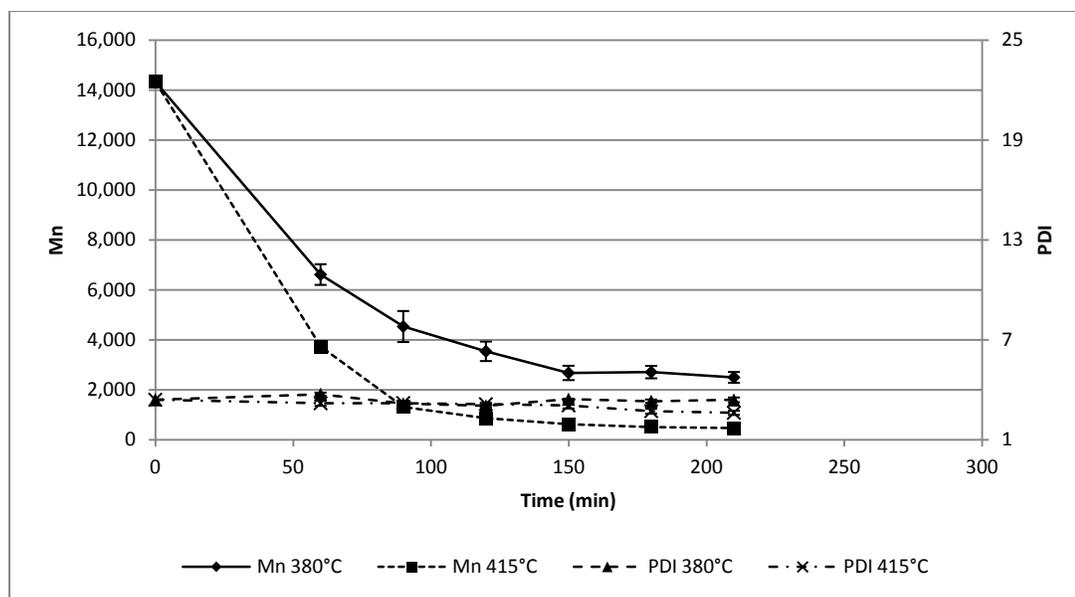
Figure 4.1 Plot of molecular weight and polydispersity vs time for LLDPE degradation in a Resin Kettle.

Table 4.2 Data of Mn and PDI vs Time for LLDPE at 380°C and 415°C as plotted in Figure 4.1

Time (min)	Mn 380°C (g/mol)	Mn 415°C (g/mol)	PDI 380°C (Mw/Mn)	PDI 415°C (Mw/Mn)
0	14331	14331	3.40	3.40
60	6612	3730	3.73	3.19
90	4532	1312	3.16	3.20
120	3539	860	3.04	3.14
150	2673	626	3.43	3.06
180	2707	511	3.31	2.71
210	2495	466	3.39	2.62
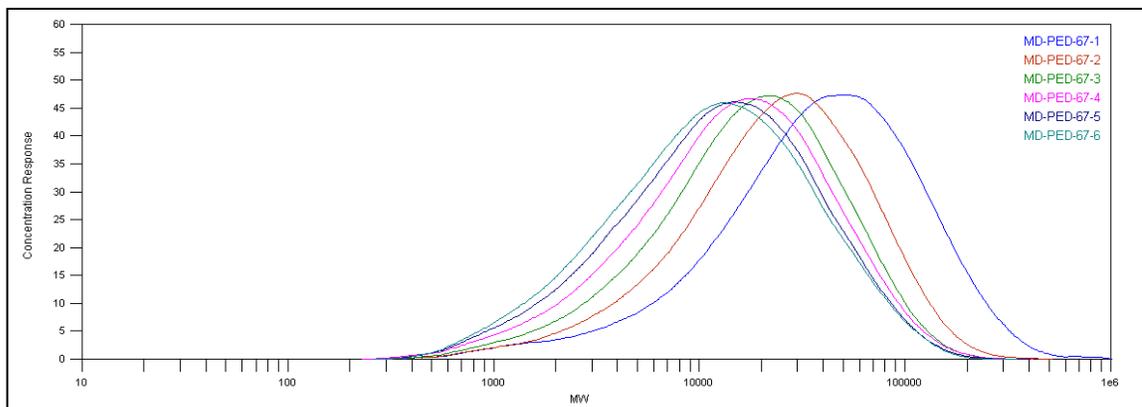
Figure 4.2 GPC chromatogram of LLDPE degradation in a Resin Kettle at 380°C
(Sample 1 – 60 min; 2 – 90 min; 3 – 120 min; 4 – 150 min; 5 – 180 min; 6 – 210 min).
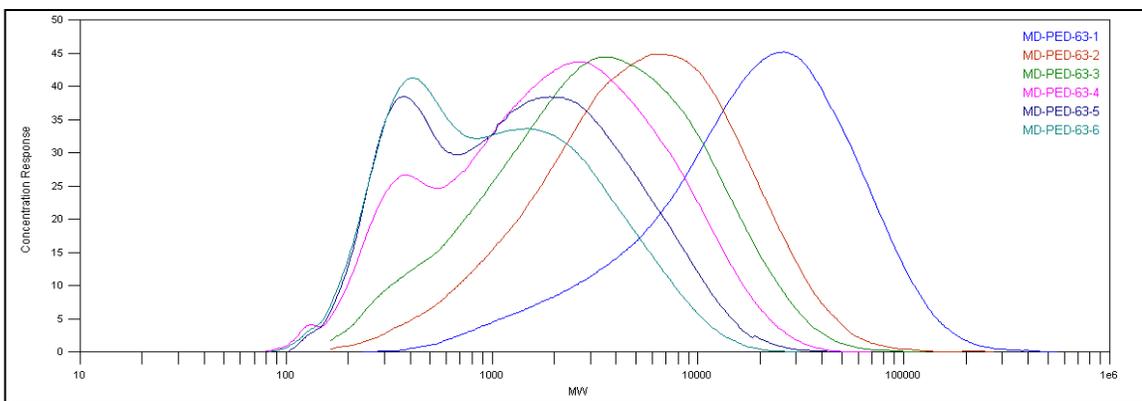
Figure 4.3 GPC chromatogram of LLDPE degradation in Resin Kettle at 415°C
(Sample 1 – 60 min; 2 – 90 min; 3 – 120 min; 4 – 150 min; 5 – 180 min; 6 – 210 min).
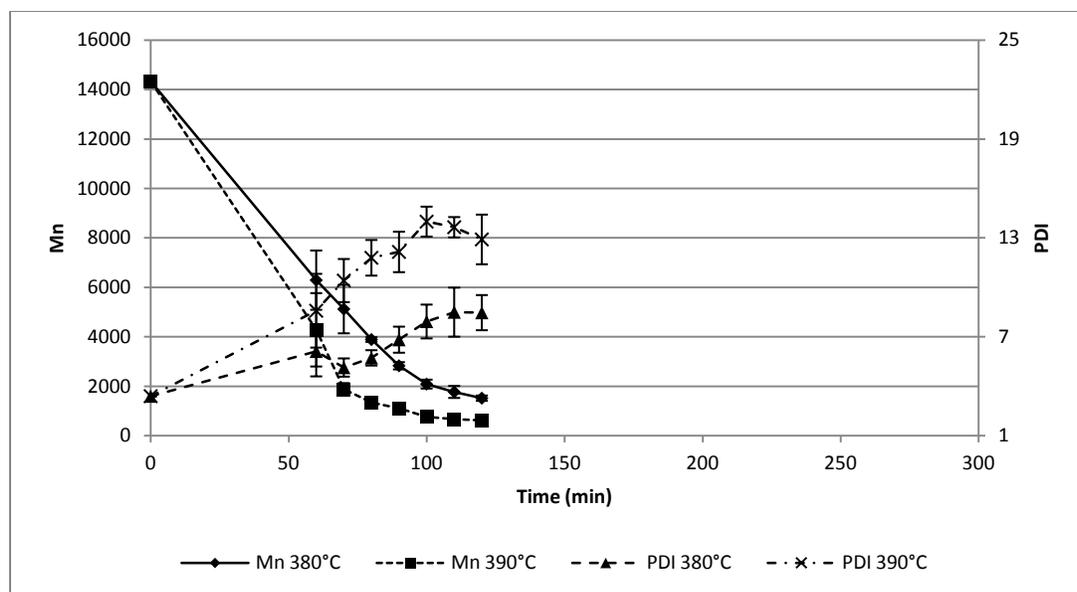
Figure 4.4 Plot of molecular weight and polydispersity vs. time for LLDPE degradation in a Resin Kettle with Si-Al catalyst.

Table 4.3 Data of Mn and PDI vs Time for LLDPE at 380°C and 390°C as plotted in Figure 4.4

Time (min)	Mn 380°C (g/mol)	Mn 390°C (g/mol)	PDI 380°C (Mw/Mn)	PDI 390°C (Mw/Mn)
0	14331	14331	3.40	3.40
60	6292	4284	6.12	8.58
70	5122	1880	5.14	10.41
80	3889	1343	5.72	11.79
90	2829	1108	6.83	12.15
100	2088	758	7.93	13.99
110	1771	672	8.50	13.65
120	1519	625	8.47	12.91

37
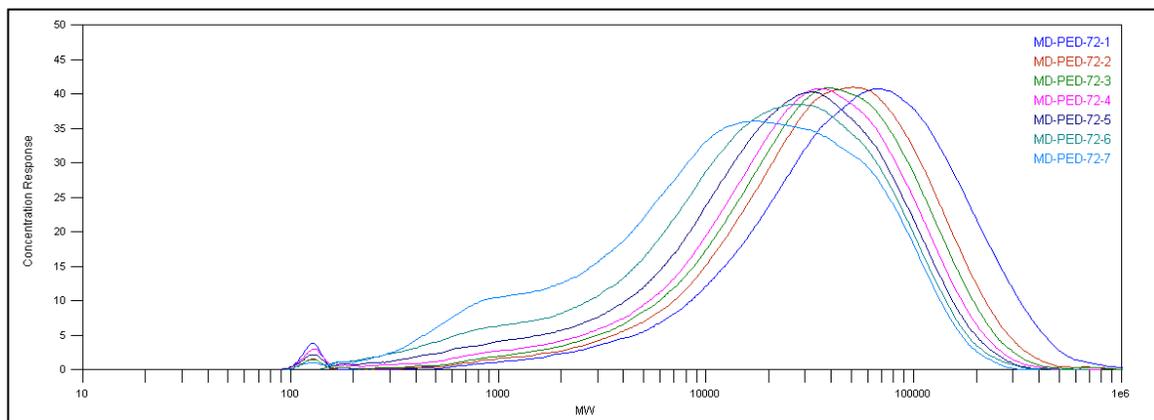
Figure 4.5 GPC chromatogram of LLDPE degradation in a Resin Kettle at 380°C with Si-Al catalyst (Sample 1 – 60 min; 2 – 70 min; 3 – 80 min; 4 – 90 min; 5 – 100 min; 6 – 110 min; 7 – 120 min).
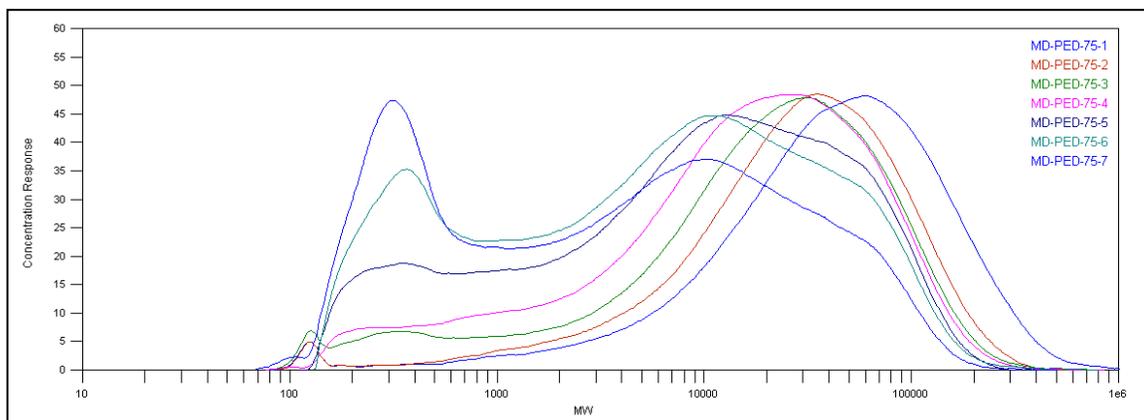
Figure 4.6 GPC chromatogram of LLDPE degradation in a Resin Kettle at 390°C with Si-Al catalyst (Sample 1 – 60 min; 2 – 70 min; 3 – 80 min; 4 – 90 min; 5 – 100 min; 6 – 110 min; 7 – 120 min).

Figures 4.2 and 4.3 are chromatograms displaying molecular weight measurements from samples taken at predetermined times during runs at 380°C and 415°C in the resin kettle. Examining the traces from the GPC measurements gives more insight into what is occurring to the material as time progresses. In Figure 4.2 at 380°C, each sample measurement shows a normally distributed curve with a peak at the average molecular weight of the sample. As time progresses the peak continuously moves to a smaller molecular weight with the distribution retaining much of its shape. Much the same is seen in Figure 4.3 at 415°C, with the exception that the polydispersity increases as the degradation progresses. At the higher degradation temperature of 415°C, two polymer populations begin to appear in the form of a shoulder on the curve causing a wider distribution. This may point to an alternate degradation pathway that is present at higher temperatures. With regards to the molecular weight, the same trend is observed with catalyst as without catalyst, see Figure 4.4. There is a rapid decrease in the molecular weight early on, and over time the rate of decrease slows down. This exponential decay has been observed in all experiments and is believed to exist for the reason outlined above. Figures 4.5 and 4.6 are the chromatograms for molecular weight measurements made on samples from runs at 380°C and 390°C with catalyst. In Figure 4.5, at the lower temperature of 380°C there is a larger population of small molecules with a molecular weight of less than 1000 g/mol. This was not seen at 380°C without catalyst (Figure 4.2), keeping in mind that the catalyst run was much shorter in duration. In Figure 4.6 at 390°C a large increase in the polydispersity of the material has occurred. The molecular weight distribution has become very broad and has gone from being unimodal to bimodal with a large population of molecules having a peak molecular weight of 300 g/mol.

39

Tables 4.2 and 4.3 lists the molecular weights and polydispersity values for LLDPE degradation at 380°C and 415°C in a resin kettle. If a comparison is made between Tables 4.2 and 4.3, when molecular weights at the same sample time are compared it appears as though the catalyst has increased the rate of degradation. It is also observed that at the higher run temperature of 390°C with catalyst (Table 4.3), the molecular weight distribution has broadened considerably as seen by the high polydispersity values. It can be concluded from this that the use of catalyst allows small fragments to be generated very rapidly before all of the high molecular weight material has been broken down. This in turn causes the molecular weight distribution to widen significantly and in-fact become bimodal. This can be seen in Figure 4.6 where the left hand side of the distribution has moved significantly toward the low molecular weight values and the right hand side of the distribution has moved very little over the course of the experiment.

4.2.2   Degradation of LLDPE Under Pressurized Conditions Using a Parr Reactor

In addition to the resin kettle, another set of reactions was carried out with LLDPE in a sealed Parr reactor. This series of experiments contrasts with the resin kettle in that no volatiles were allowed to escape during the course of the reaction. In these experiments the pressure in the reactor increased as more and more volatile components began to fill the headspace of the reactor. It is important to note that the reactor was not pressurized at the beginning of the experiment. The polymer was charged to the reactor and then the reactor was sealed so that when heating was started the pressure inside the reactor was at atmospheric pressure, or 0 psig. When the experiment had concluded the

resulting pressure was read off of a pressure gauge mounted on top of the reactor as seen in Figure 3.2.

Table 4.4 lists the run temperature, the run time and the resulting pressure accumulation that resulted from Parr experiments without catalyst. Table 4.5 lists the same for experiments conducted with catalyst. The data shows that there was a marked difference between the pressure generated by the experiments conducted with and without catalyst. Table 4.4 shows that without catalyst at 380°C, the pressure initially increased by 17.5 psi from 0 minutes to 120 minutes and then increased moderately over the next 60 minutes to 10 psi. Similarly at 380°C with catalyst the same behaviour occurs as seen in Table 4.5. The pressure initially builds to 160 psi in the first 120 minutes, and then it holds constant for the next 60 minutes. Conversely, at 415°C both with and without catalyst the pressure increase shows no sign of abating from the beginning of the experiment right through to the end with the catalyzed reaction far outpacing the uncatalyzed reaction in terms of pressure build-up. This trend fits that observed in the resin kettle experiments, namely that the catalyst allows small molecules, which pressurize the reactor, to be generated very quickly. Comparing the pressure at 120 minutes shows that the catalyzed reaction generates 500% more pressure than the non-catalyzed reaction, whereas a comparison of pressures at 180 minutes shows only a 300% difference.

There were some unexpected trends with the LLDPE in the Parr reactor, namely that 380°C without catalyst produced a lower molecular weight than with catalyst. Table 4.6 shows the molecular weight and polydipsersity for LLDPE in the Parr reactor at 380°C and 415°C. Table 4.7 shows the same with catalyst. A comparison of the two tables at

380°C shows that the molecular weight is much higher for the run with catalyst. This result is counterintuitive and unexpected. At 415°C the expected trend is restored with the catalyst run producing much lower molecular weight material.

Table 4.4 Pressure accumulation in the Parr reactor during LLDPE degradation without catalyst

Temperature (°C)	Time (min)	P(psi)
380	0	0
380	120	17
380	180	22
380	300	27.5
415	0	0
415	120	90
415	180	160
415	300	435

Table 4.5 Pressure accumulation in the Parr reactor during LLDPE degradation with catalyst

Temperature (°C)	Time (min)	P(psi)
380	0	0
380	120	160
380	150	160
380	180	160
415	0	0
415	120	544
415	150	640
415	180	780
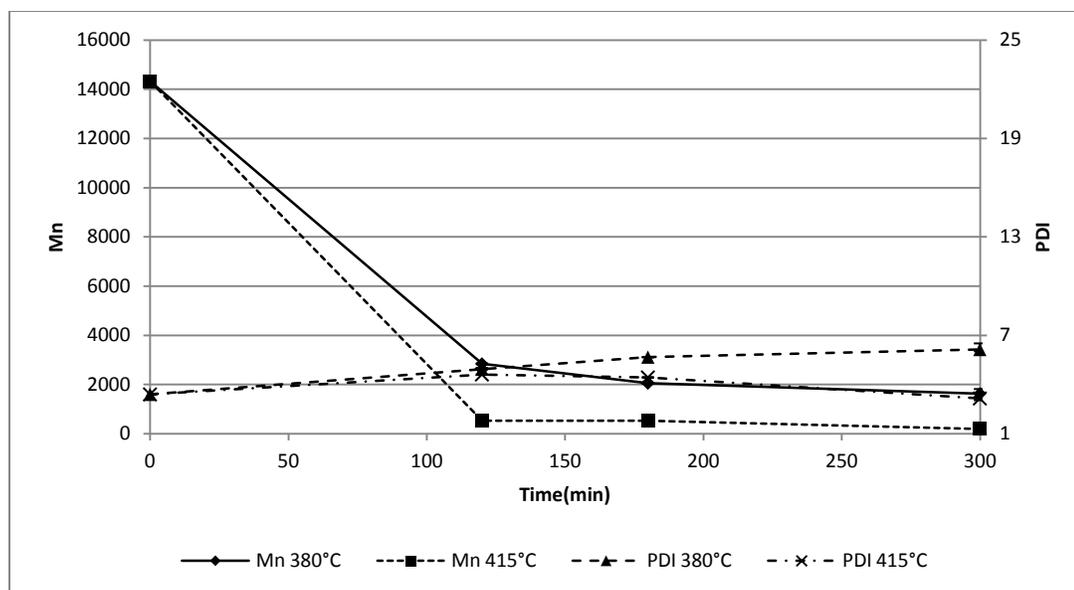
Figure 4.7 Plot of molecular weight and polydispersity vs time for LLDPE degradation in Parr reactor.

Table 4.6 Data of Mn and PDI vs Time for LLDPE at 380°C and 415°C as plotted in Figure 4.7

Time (min)	Mn 380°C (g/mol)	Mn 415°C (g/mol)	PDI 380°C (Mw/Mn)	PDI 415°C (Mw/Mn)
0	14331	14331	3.40	3.40
120	2843	535	4.94	4.61
180	2053	529	5.67	4.44
300	1629	193	6.14	3.15
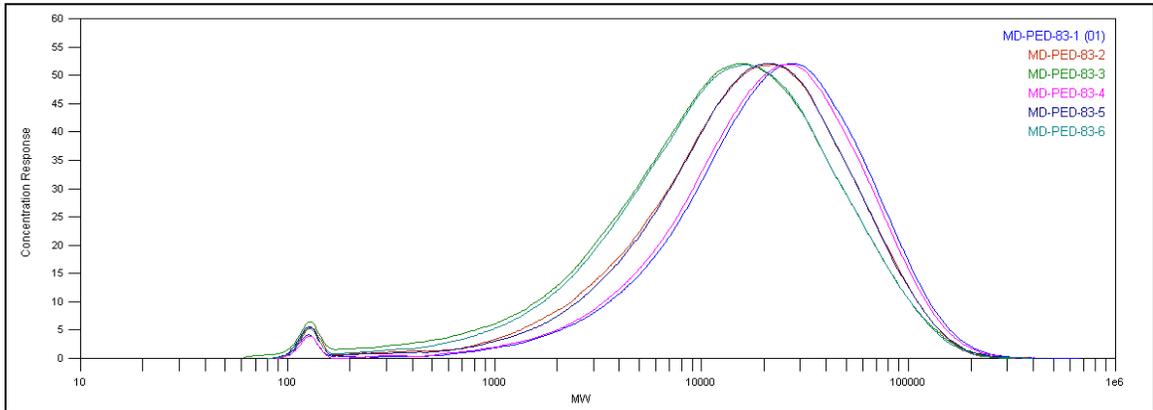
Figure 4.8 GPC chromatogram of LLDPE degradation in a Parr reactor at 380°C (Sample 1,2 – 120 min; 3,4 – 180 min; 5,6 – 300 min).
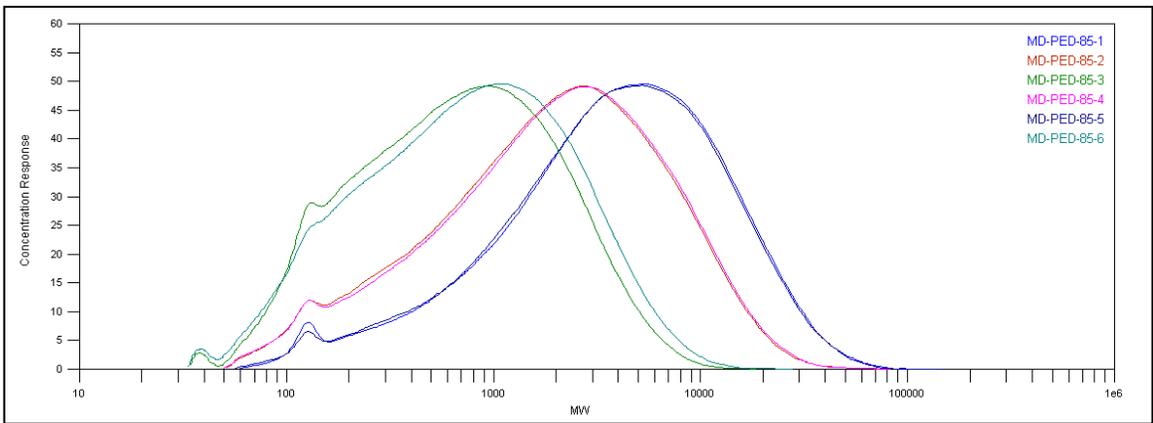
Figure 4.9 GPC chromatogram of LLDPE degradation in a Parr reactor at 415°C (Sample 1,2 – 120 min; 3,4 – 180 min; 5,6 – 300 min).
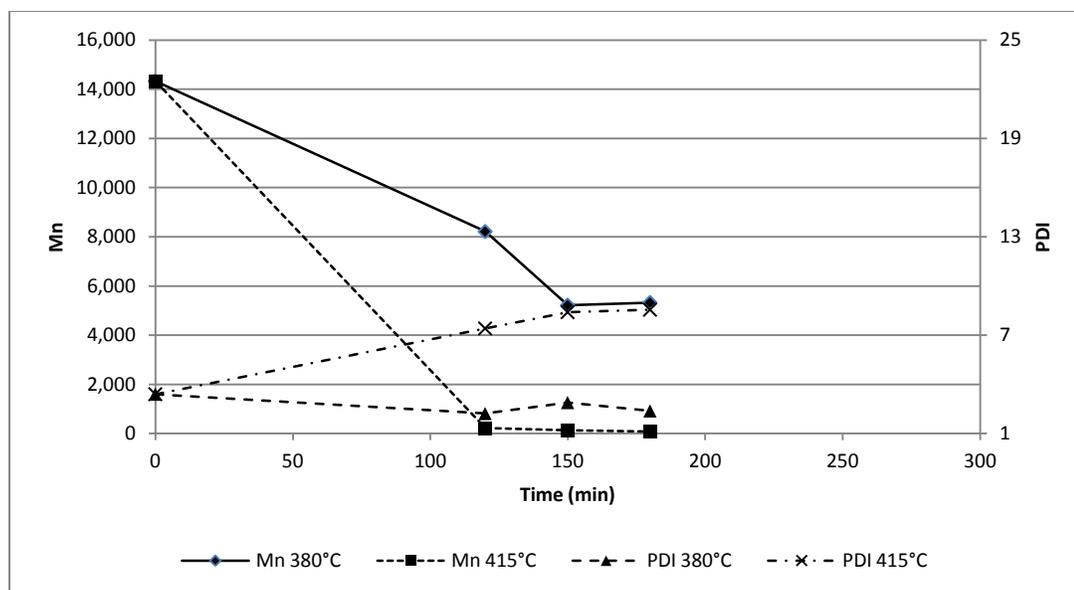
Figure 4.10 Plot of molecular weight and polydispersity vs time for LLDPE degradation in a Parr reactor with Si-Al catalyst.

Table 4.7 Data of Mn and PDI vs Time for LLDPE at 380°C and 415°C as plotted in Figure 4.10

Time (min)	Mn 380°C (g/mol)	Mn 415°C (g/mol)	PDI 380°C (Mw/Mn)	PDI 415°C (Mw/Mn)
0	14331	14331	3.40	3.40
120	8214	222	2.22	7.41
150	5219	130	2.89	8.40
180	5324	78	2.38	8.55
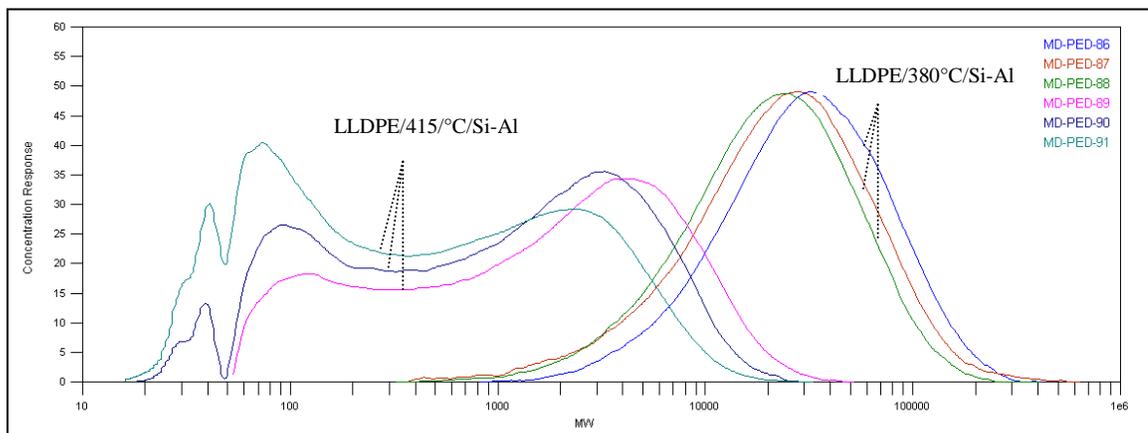
**Figure 4.11** GPC chromatogram of LLDPE degradation in a Parr reactor with Si-Al catalyst (Sample 86 – 380°C/120 min; 87 – 380°C/150 min; 88 – 380°C/180 min; 89 – 415°C/120 min, 90 – 415°C/150 min, 91 – 415°C/180 min)

4.3 Thermal Degradation of HDPE

In order to complete the study of thermal degradation of linear polyethylenes, HDPE was also degraded using the resin kettle and Parr reactor setups as had been done with LLDPE. The experimental conditions exactly matched those used for the degradation experiments involving LLDPE so that a direct comparison could be made as to the effect of material type on wax product properties and degradation kinetics. As will be shown, the results with HDPE closely resemble the results obtained with LLDPE although they do differ in some aspects. It has been generally observed in this work that all things being equal, HDPE will degrade to a slightly higher molecular weight than LLDPE. This trend was seen primarily for reactions at 415°C. The polydispersity for HDPE was much higher than LLDPE but only for reactions at 380°C.

4.3.1 Degradation of HDPE using a Resin Kettle Reactor

Table 4.8 shows the molecular weight and polydispersity for HDPE in the resin kettle at 380°C and 415°C without catalyst. Table 4.9 shows the same for experiments conducted with catalyst. We observe here, as with the LLDPE experiments, that using catalyst speeds up the process of degradation, while at the same time increasing polydispersity. Figures 4.13 and 4.14 show the GPC traces for HDPE samples taken in the resin kettle at 380°C and 415°C. These GPC traces closely resemble those for LLDPE in the same reactor setup at the same conditions. It is observed that HDPE produces slightly higher molecular weights under the same conditions. It can also be noted in Table 4.9 that there is little difference in the overall degradation kinetics and product properties between 380°C and 390°C as results are similar. This can be clearly

observed in Figure 4.15 where the data from the two runs at different temperatures overlap. However when we examine the GPC traces in Figures 4.16 and 4.17 we note that the they differ between these operating temperatures, with the higher temperature producing two polymer populations that are mores distinctly defined. In contrast, at the lower temperature the starting material is less degraded to produce a more mono-modal distribution that is wider.   It is observed that like LLPDE, the catalyst has enabled the rapid production of low molecular weight species, particularly at higher temperatures. This can be seen by the fact that the left hand side of the GPC traces has been skewed down to the low molecular weights while the right hand side has barely moved from its original position. When Figure 4.17 is compared to 4.6, it can be seen that the lack of degradation at the high molecular weights is even more pronounced with HDPE than it was with LLDPE, however LLDPE produced a larger amount of low molecular weight species.
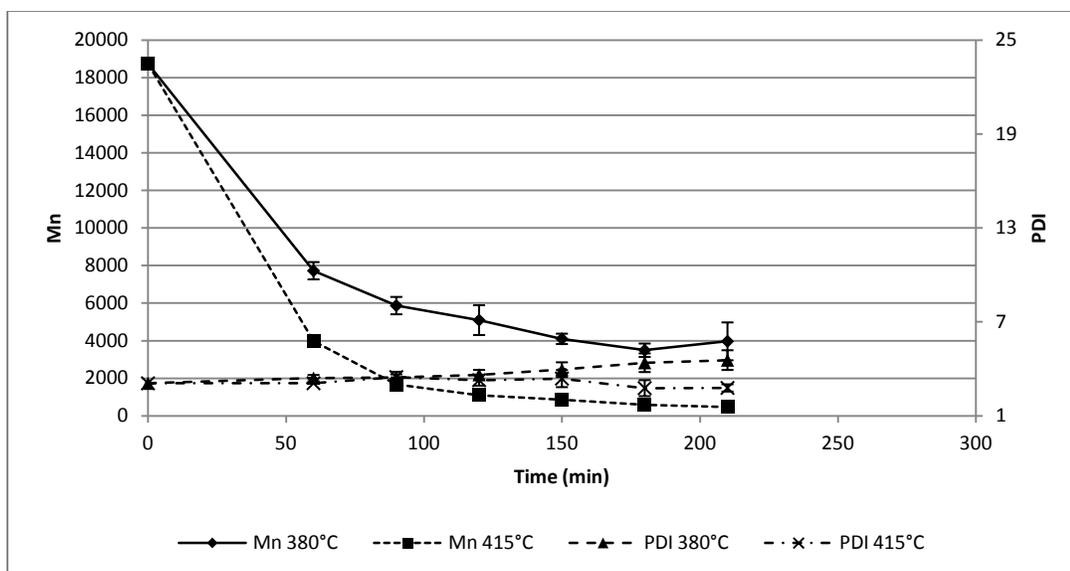
Figure 4.12 Plot of molecular weight and polydispersity vs time for HDPE degradation in a Resin Kettle.

Table 4.8 Data of Mn and PDI vs Time for HDPE at 380°C and 415°C as plotted in Figure 4.12

Time (min)	Mn 380°C (g/mol)	Mn 415°C (g/mol)	PDI 380°C (Mw/Mn)	PDI 415°C (Mw/Mn)
0	18743	18743	3.08	3.08
60	7725	3970	3.41	3.08
90	5868	1674	3.45	3.48
120	5094	1104	3.63	3.28
150	4099	860	3.95	3.38
180	3493	584	4.39	2.77
210	3967	473	4.56	2.78
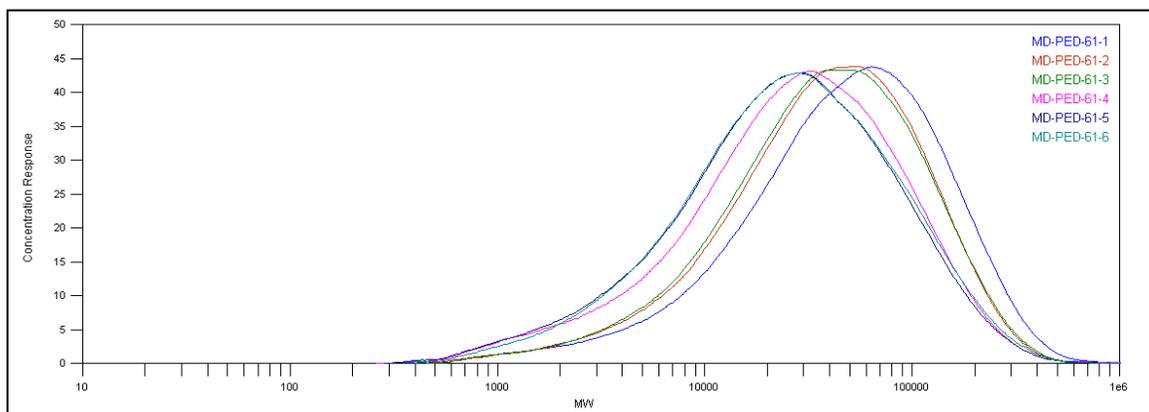
Figure 4.13 GPC chromatogram of HDPE degradation in Resin Kettle at 380°C (Sample 1 – 60 min, 2 – 90 min, 3 – 120 min, 4 – 150 min, 5 – 180 min, 6 – 210 min)
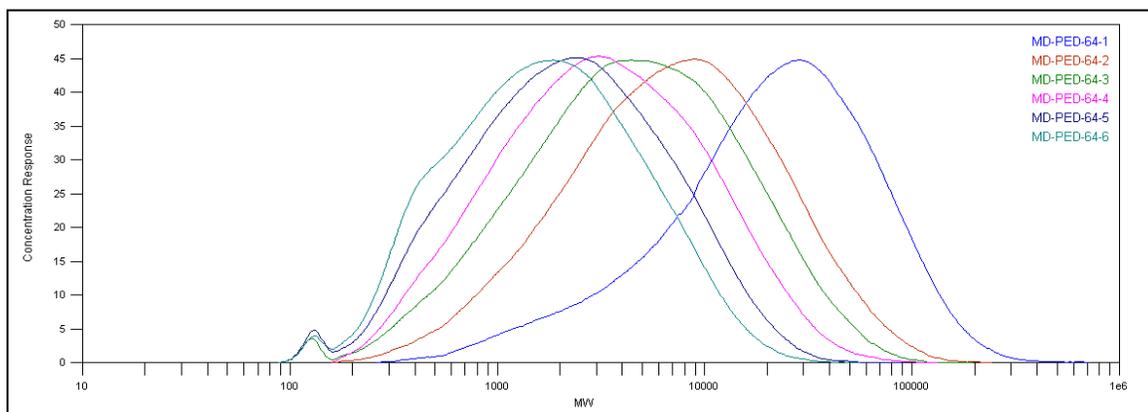
**Figure 4.14** GPC chromatogram of HDPE degradation in Resin Kettle at 415°C (Sample 1 – 60 min, 2 – 90 min, 3 – 120 min, 4 – 150 min, 5 – 180 min, 6 – 210 min)
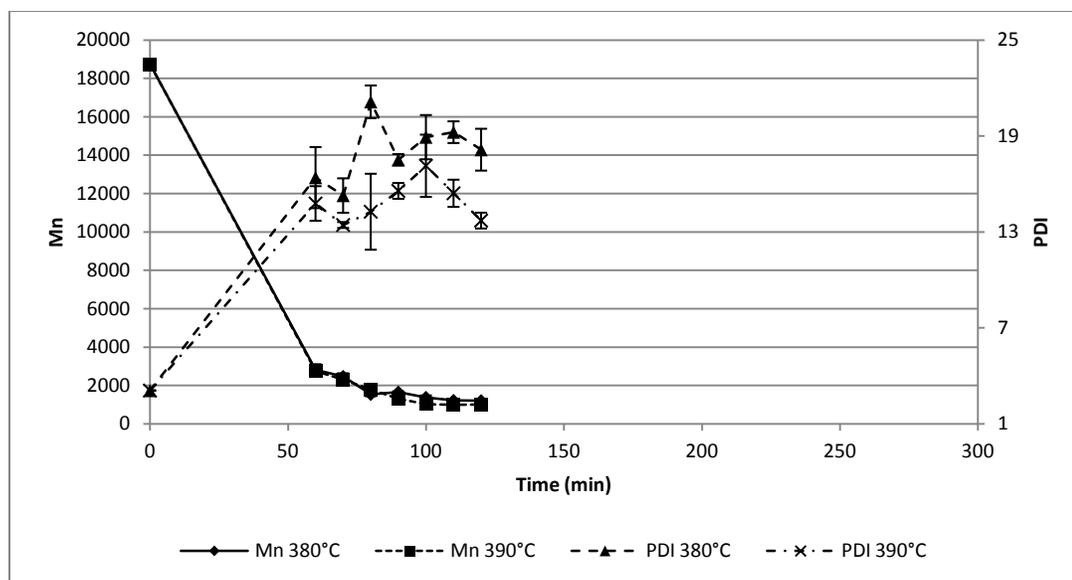
Figure 4.15 Plot of molecular weight and polydispersity vs time for HDPE degradation in a Resin Kettle reactor with Si-Al catalyst.

Table 4.9 Data of Mn and PDI vs Time for HDPE at 380°C and 390°C as plotted in Figure 4.4

Time (min)	Mn 380°C (g/mol)	Mn 390°C (g/mol)	PDI 380°C (Mw/Mn)	PDI 390°C (Mw/Mn)
0	18743	18743	3.08	3.08
60	2809	2743	16.40	14.78
70	2469	2307	15.28	13.43
80	1530	1781	21.14	14.26
90	1649	1304	17.51	15.57
100	1378	1026	18.93	17.14
110	1217	991	19.24	15.42
120	1207	1007	18.14	13.71
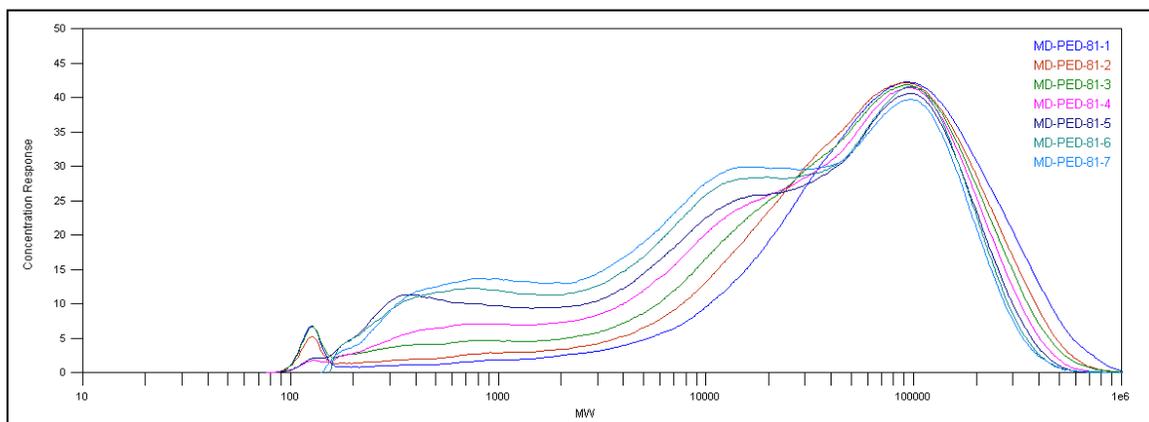
Figure 4.16 GPC chromatogram of HDPE degradation in a Resin Kettle reactor at 380°C with Si-Al catalyst (Sample 1 – 60 min; 2 – 70 min; 3 – 80 min; 4 – 90 min; 5 – 100 min; 6 – 110 min; 7 – 120 min).
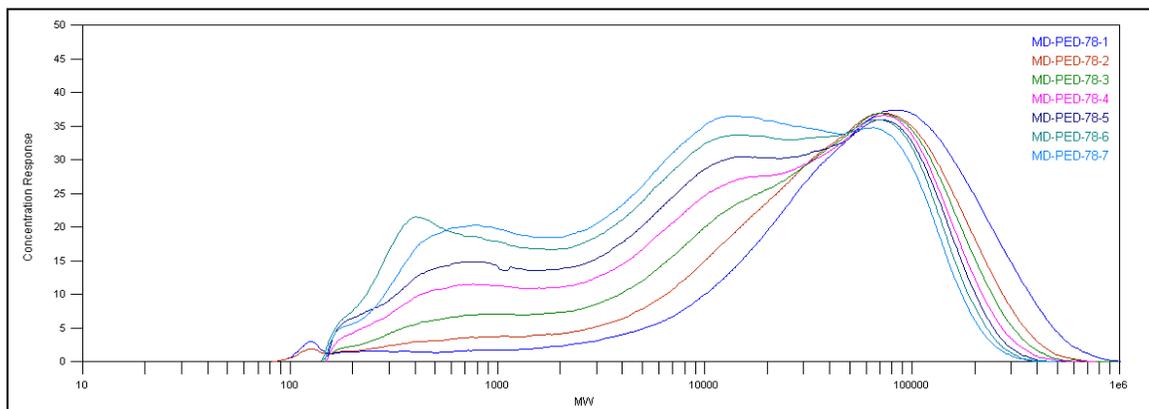
Figure 4.17 GPC chromatogram of HDPE degradation in a Resin Kettle reactor at 390°C with Si-Al catalyst (Sample 1 – 60 min; 2 – 70 min; 3 – 80 min; 4 – 90 min; 5 – 100 min; 6 – 110 min; 7 – 120 min).

4.3.2   Degradation of HDPE in a Parr Reactor

HDPE degradation was carried out in a sealed Parr reactor where volatile products were contained within the reactor, which resulted in pressure accumulation. Table 4.10 shows the pressure accumulation during the degradation of HPDE without catalyst at various temperatures and run times. Table 4.11 shows the same for experiments with catalyst. At 380°C without catalyst, Table 4.10, the pressure increased to 15 psi and then increased very little as time progressed to 20 psi. At this same temperature with catalyst the pressure increased to a plateau of 170 psi and remained there for the remainder of the experiment. At 415°C however no plateau was observed with or without catalyst, with pressures continuing to rise significantly over the reaction. The pattern of pressure accumulation for HDPE closely resembles that of LLDPE both with and without catalyst indicating that the higher temperature, as expected, leads to a greater degree of degradation as observed by the higher pressures produced.

Figures 4.19 and 4.20 show the GPC traces of degraded HPDE samples without catalyst in the Parr reactor at 380°C and 415°C respectively. Figure 4.22 shows the same for experiments conducted with catalyst. Comparing Figures 4.18 and 4.21 we observe, as before with LLDPE, that the use of catalyst greatly accelerates the rate of degradation at higher temperatures (415°C). Again we also observe that at 415°C with catalyst the polydispersity of the product is higher than without catalyst. In comparing the GPC chromatograms of HDPE and LLDPE in the Parr reactor we see virtually identical results. The only difference can be seen in the trace showing degradation at 415°C with catalyst (Figure 4.22), where HDPE produced slightly fewer low molecular weight

products. Despite this the shapes of the GPC traces for HPDE (Figures 4.19- 4.21) are virtually identical to LLDPE (Figures 4.8 - 4.11).

Table 4.10 Pressure accumulation in the Parr reactor during HDPE degradation without catalyst

Temperature (°C)	Time (min)	P(psi)
380	0	0
380	120	15.5
380	180	20
380	300	20
415	0	0
415	120	56
415	180	115
415	300	290

Table 4.11 Pressure accumulation in the Parr reactor during HDPE degradation with catalyst

Temperature (°C)	Time (min)	P(psi)
380	0	0
380	120	170
380	150	180
380	180	170
415	0	0
415	120	508
415	150	620
415	180	720
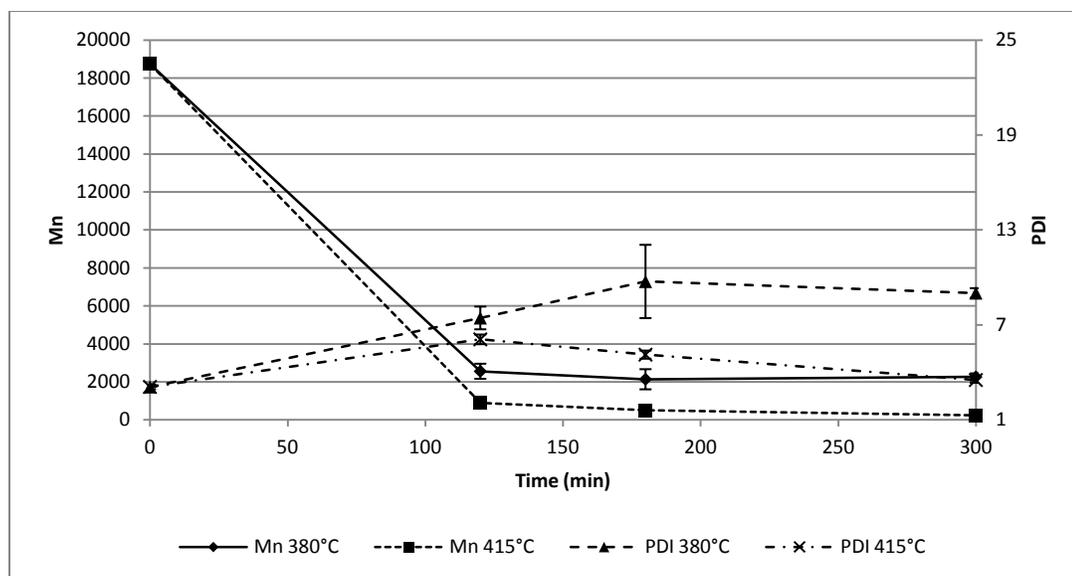
Figure 4.18 Plot of molecular weight and polydispersity vs time for HDPE degradation in a Parr reactor.

Table 4.12 Data of Mn and PDI vs Time for HDPE at 380°C and 415°C as plotted in Figure 4.18

Time (min)	Mn 380°C (g/mol)	Mn 415°C (g/mol)	PDI 380°C (Mw/Mn)	PDI 415°C (Mw/Mn)
0	18743	18743	3.08	3.08
120	2558	884	7.44	6.09
180	2137	510	9.75	5.12
300	2259	237	9.02	3.52
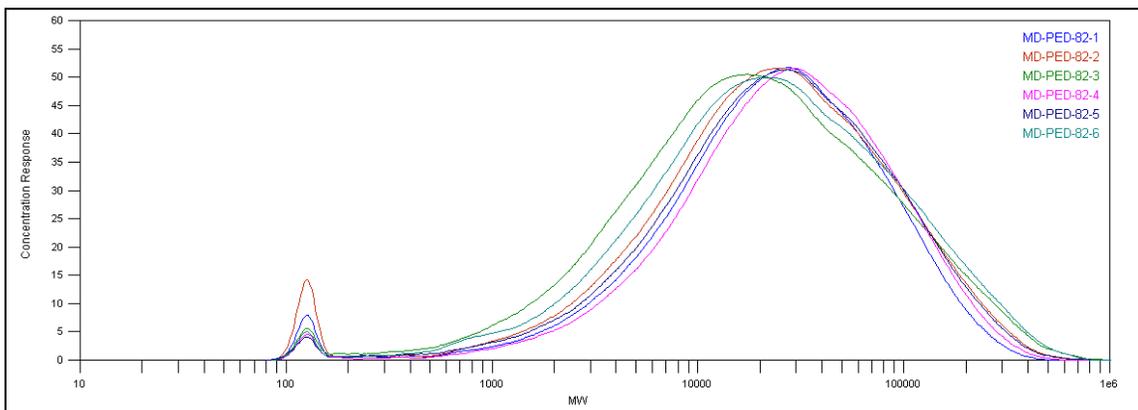
Figure 4.19 GPC chromatogram of HDPE degradation in a Parr reactor at 380°C (Sample 1,4 – 120 min; 2,5 – 180 min; 3,6 – 300 min)
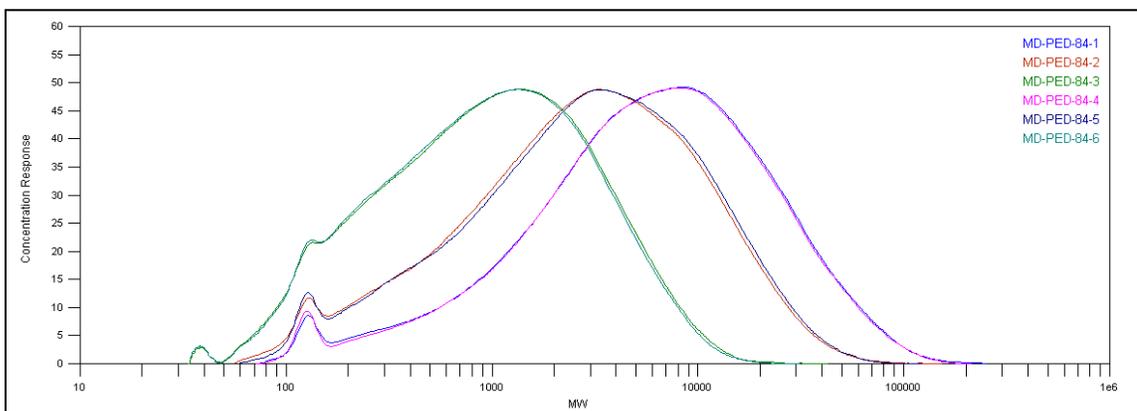
Figure 4.20 GPC chromatogram of HDPE degradation in a Parr reactor at 415°C (Sample 1,4 – 120 min; 2,5 – 180 min; 3,6 – 300 min)
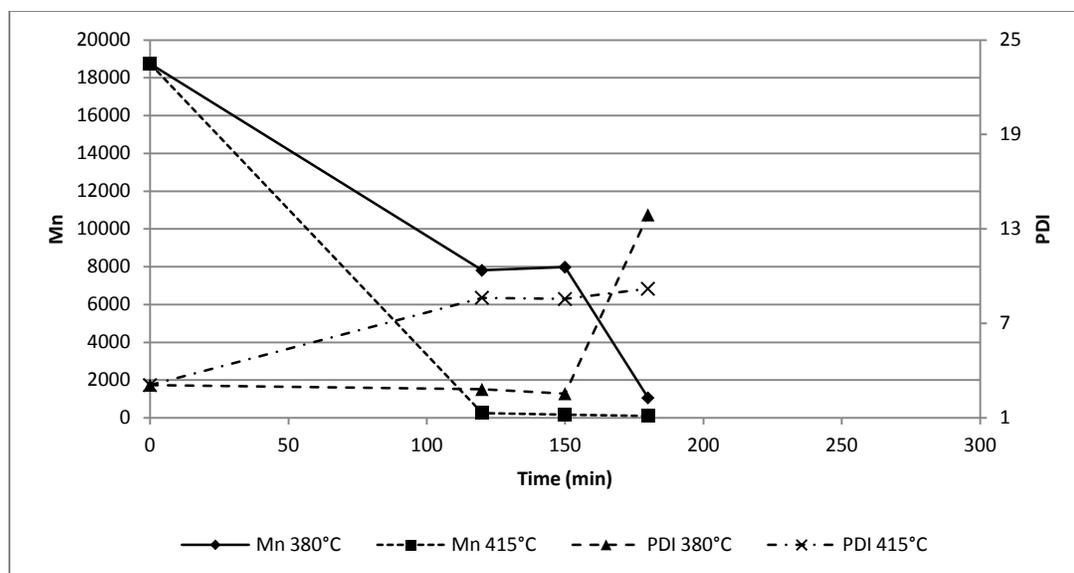
Figure 4.21 Plot of molecular weight and polydispersity vs time for HDPE degradation in a Parr reactor with Si-Al catalyst.

Table 4.13 Data of Mn and PDI vs. Time for HDPE at 380°C and 415°C as plotted in Figure 4.21

Time (min)	Mn 380°C (g/mol)	Mn 415°C (g/mol)	PDI 380°C (Mw/Mn)	PDI 415°C (Mw/Mn)
0	18743	18743	3.08	3.08
120	7809	256	2.81	8.63
150	7976	165	2.54	8.55
180	1056	104	13.9	9.2
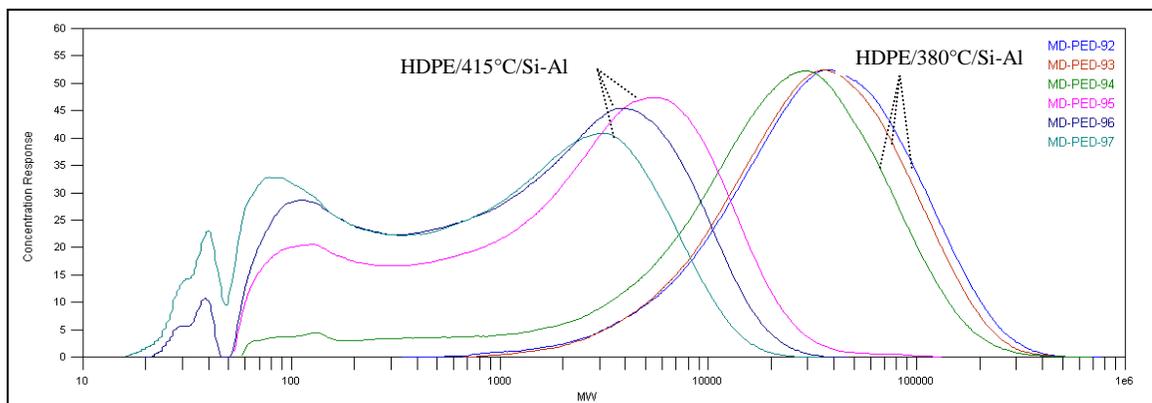
**Figure 4.22** GPC chromatogram of HDPE degradation in a Parr reactor with Si-Al catalyst (Sample 92 – 380°C/120 min; 93 – 380°C/150 min; 94 – 380°C/180 min; 95 – 415°C/120 min; 96 – 415°C/150 min; 97 – 415°C/180 min)

4.4 Characterization of Physical Properties of Degradation Products

As originally set out in the objectives of this work, it is desired to take polyethylene of high molecular weight and thermally degrade it down causing the original polymer to break into smaller fragments. The smaller fragments with lower molecular weight constitute a waxy residue, and it is this wax and its potential applications that are of interest provided it displays acceptable physical properties. To that end, the physical properties of the degradation products were analyzed with differential scanning calorimetry (DSC) to determine melting point and with a rheometer to determine the flow characteristics. A narrowly distributed commercially available polyethylene wax was also characterized for comparison. In addition to comparing the physical properties to commercial distilled waxes, these analyses also allow inferences to be made about the process of degradation and the materials that are produced under certain experimental conditions.

4.4.1 DSC Analysis of Degradation Products

Due to the large number of samples produced in this study, only a subset of the materials, most comparable to the commercial reference, were analyzed. The commercial material, which is a polyethylene wax (Figure 4.23) has a molecular weight of approximately 725 and narrow molecular weight distribution, which in turn results in a sharp melting point. Also included in the analysis are measurements of the starting materials so that the change in melting point can be seen over the course of the degradation. Only waxes produced without catalyst and in the Parr reactor, under pressure, were characterized as these had the narrowest molecular weight distribution of

the materials produced and the lowest molecular weights, and so most resembled the commercial wax sample.

It is readily apparent from the DSC traces of the starting materials (Figure 4.24 and 4.25) that the peak melting point is well defined for LLDPE and even more so for HDPE. This is in all likelihood due to the crystallinity of the material. HDPE having less branching than LLDPE, results in a more crystalline solid, which in turn results in a sharper peak melting point.

Examining the products of LLDPE degradation at 415°C (Figures 4.26 and 4.27) there is a complete lack of a well defined peak melting point, despite the fact that the polydispersity does not differ significantly from the original staring material. Consequently an analysis of the DSC traces for HDPE (Figures 4.28 and 4.29) shows a similar lack of a well defined peak melting point, although the peaks are better defined than with LLDPE. This is consistent with what was observed in the GPC analysis which showed that the HPDE undergoes less degradation than LLDPE under similar conditions. This should result in a higher melting point for HDPE as is observed in the DSC data.

In conclusion, the materials produced had melting points that were less well defined than commercially produced distilled waxes. This is understandable because no distillation had been applied to the degradation products. Yet the results show that the raw materials produced overlap with the desired properties and so through distillation, narrowly distributed waxes similar to commercial samples, could be produced.
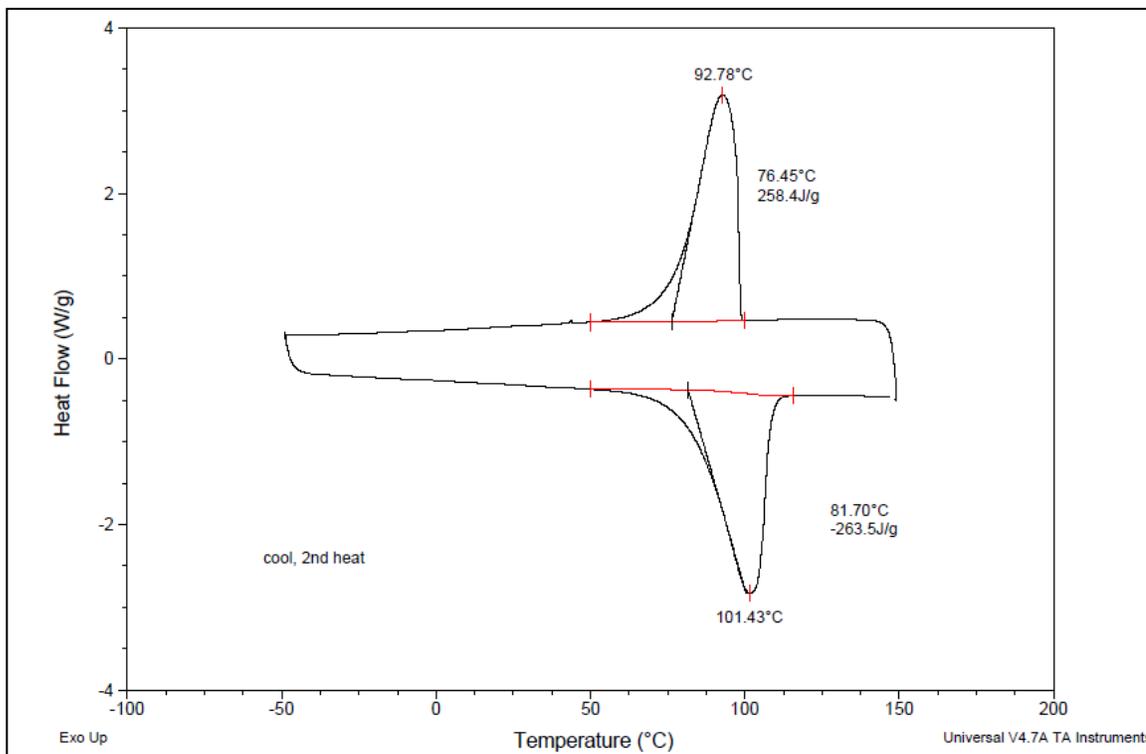
Figure 4.23 DSC Trace of Polywax 725
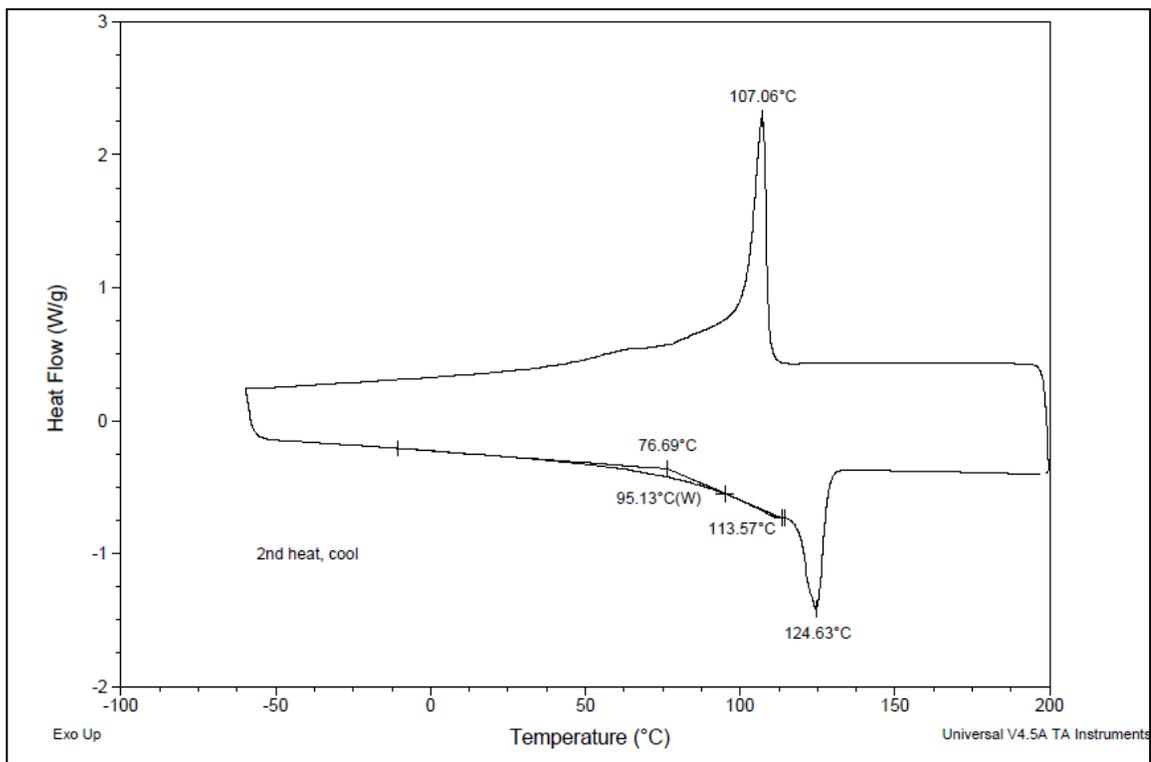
Figure 4.24 DSC Trace of LLDPE starting material
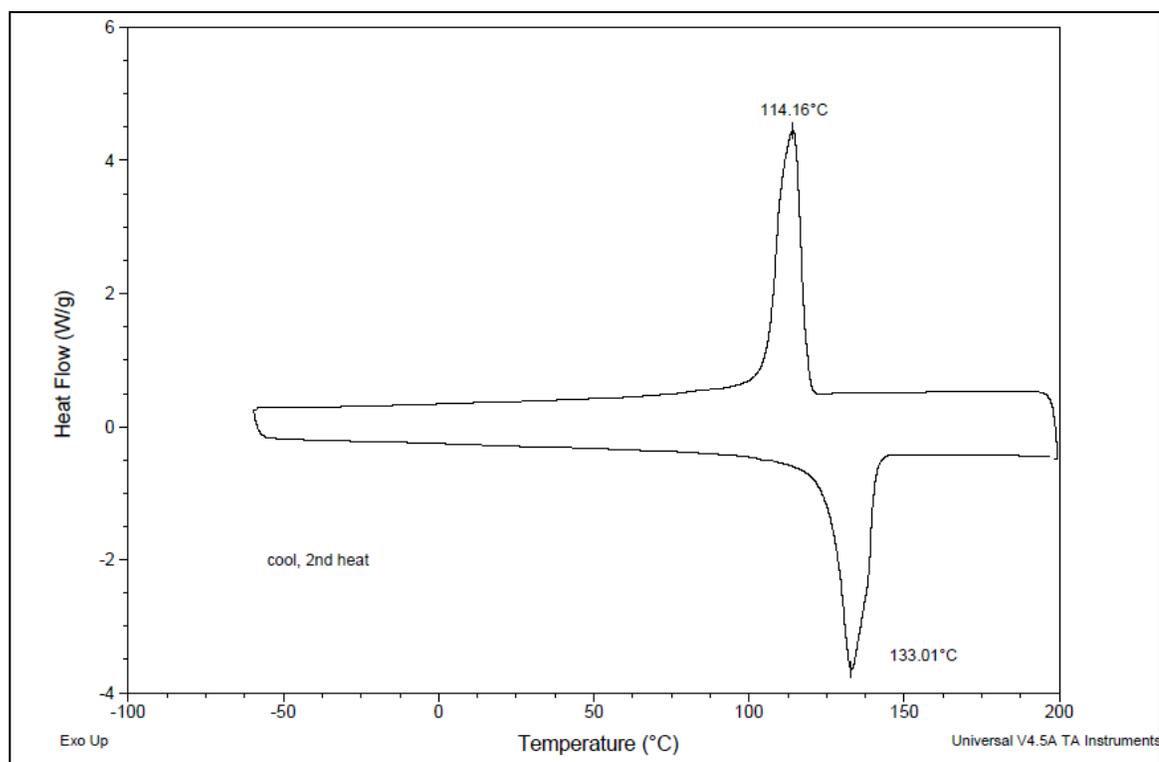
Figure 4.25 DSC Trace of HDPE starting material

64
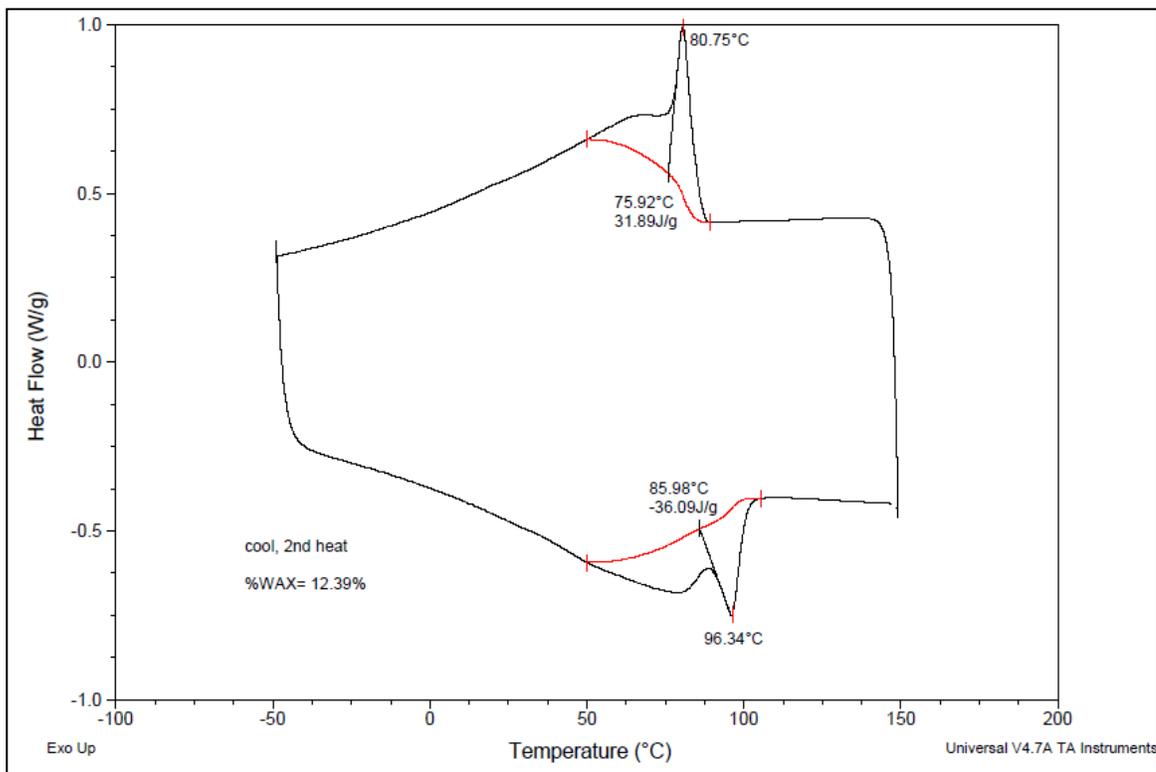
Figure 4.26 DSC Trace of product from degradation of LLDPE/415°C/Parr/180min
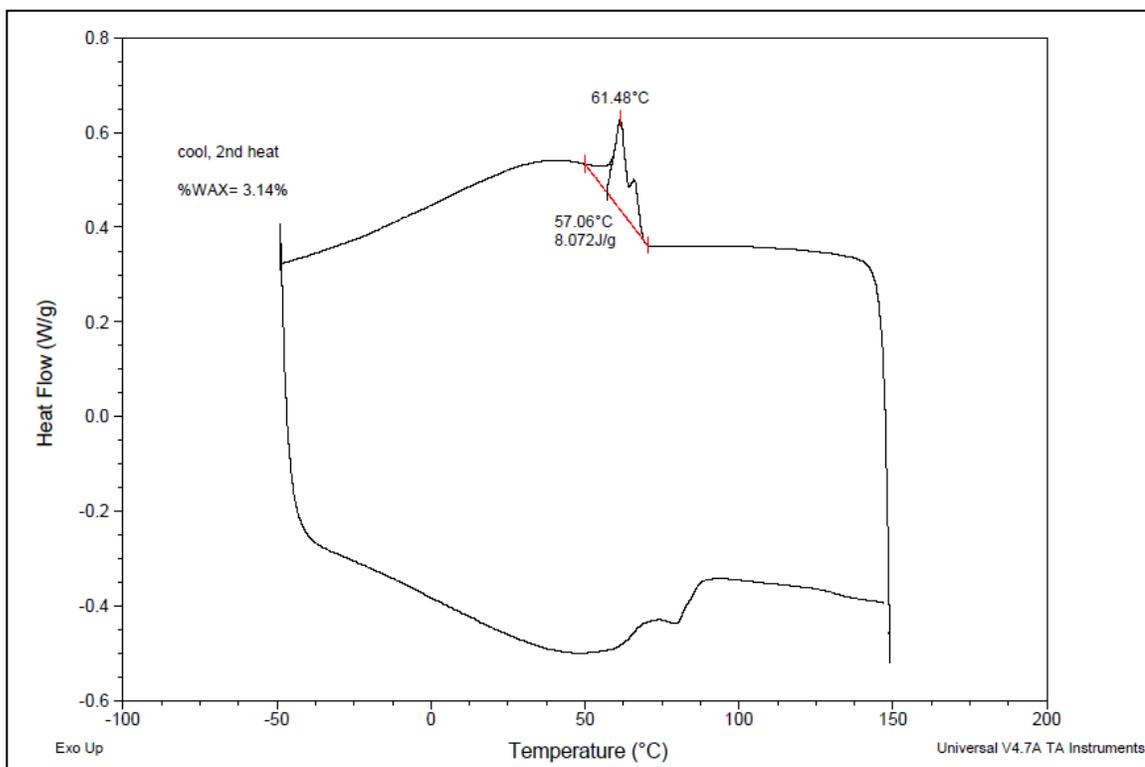
Figure 4.27 DSC Trace of product from degradation of LLDPE/415°C/Parr/300min
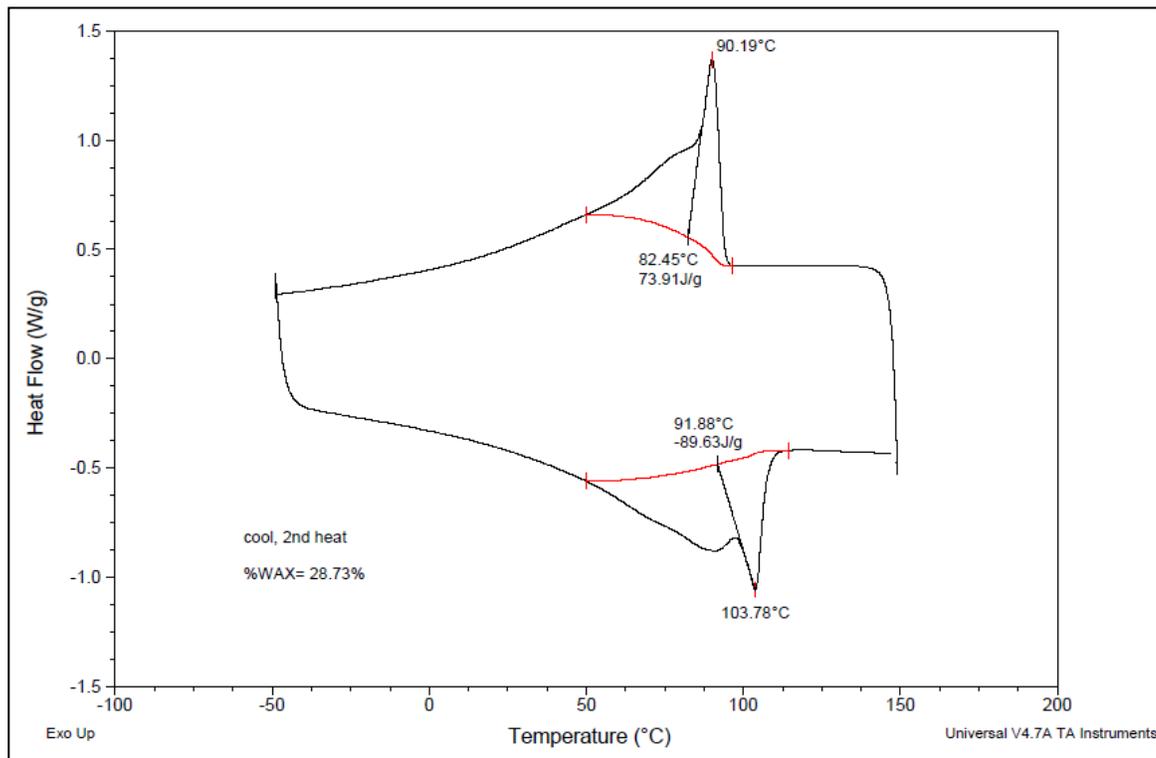
Figure 4.28 DSC Trace of product from degradation of HDPE/415°C/Parr/180min
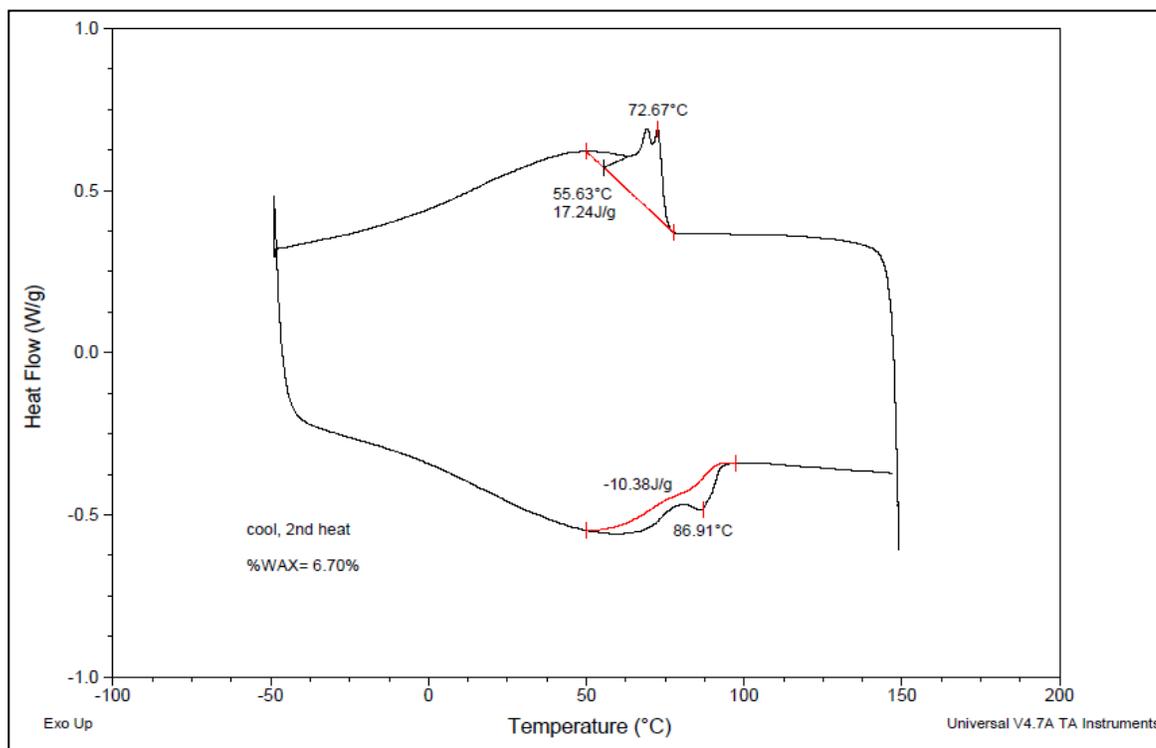
Figure 4.29 DSC Trace of product from degradation of HDPE/415°C/Parr/300min

4.4.2 Rheological Analysis of Products

Like the melting point analysis, the rheology of the degradation products also gives insight into the materials produced. A similar subset of materials that were analyzed by DSC were also analyzed for viscosity, with the addition of one sample generated with the resin kettle. The resin kettle sample was added because of its low polydispersity (2.78) despite its higher molecular weight (1226). The other samples were all Parr generated with no catalyst, however the 240 min sample was dropped in favour of the 60 min sample. The instrument starts measuring the viscosity at a preset high temperature of 140°C and continues measuring the viscosity intermittently until it reaches a preset low temperature of 40°C. From this measurement method the crystallization temperature can be observed when the viscosity begins to climb higher as the temperature decreases. Figures 3.40 and 3.41 show the rheology measurements made on the degradation products. Figure 3.41 is a zoom in of Figure 3.40. It offers more discrimination in terms of the precise temperature at which the onset of crystallization occurs. Surprisingly, the resin kettle sample with high molecular weight and low polydispersity exhibits the lowest viscosity and crystallization temperature of all the samples. As it turns out the products of degradation with the closest viscosity profile to the commercial PW-725 was LLDPE run at 415°C for 60 min and HDPE run at 415°C for 120 min.
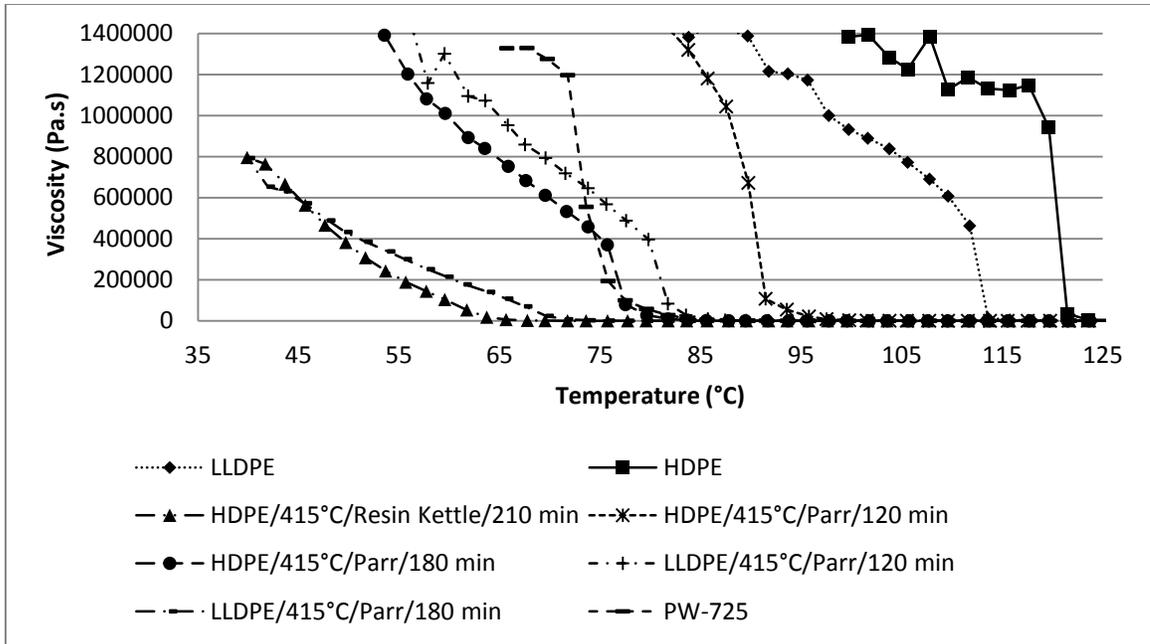
**Figure 4.30**Viscosity of Degradation Products at Various Temperatures as Measured by a Rheometer (Large viscosity Range)
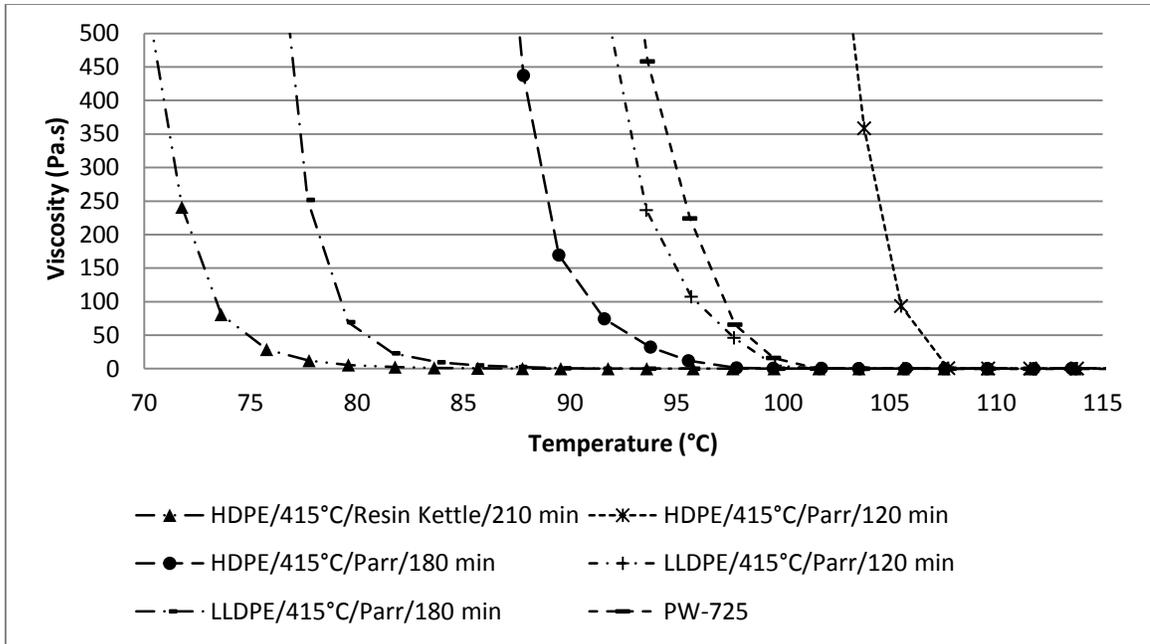
Figure 4.31 Viscosity of Degradation Products at Various Temperatures as Measured by a Rheometer (Small viscosity Range)

4.5   Branching Analysis NMR

All previous characterization methods that were performed have either measured the molecular weight via high temperature gel permeation chromatography (GPC) or physical properties via differential scanning calorimetry (DSC) and rheology measuremenets. Based on these methods only inferences can be made as to what the physical structure is of the materials being produced. In order to address this, a branching analysis using Carbon-13 NMR was performed. Ideally, the objective would be to produce a straight chain poyethyelene via degradation with no branching in it.

As with the GPC measurements, the NMR measurements also proved to be demanding in that polyethyelenes of even fairly low molecular weight are completely insoluble at room temperature. As a result elevated temperatures were used to both prepare the sample and make the measurement. Most samples adequately went into solution at 75°C with benzene as the solvent. Other samples proved more difficult to dissolve and required a higher temperature of approximately 105°C to go into solution. The elevated temperature in turn required a change in the solvent used. Benzene was no longer sufficient due to its boiling point of 80°C, so toluene with a boiling point of 110°C was used. Due to the cost prohibitive nature of performing the analysis only a select number of samples were chosen, all of which were taken from experiments conducted in the Parr reactor.

Table 4.5 lists the samples analyzed and the conditions under which they were run. From Table 4.3 in combination with Figure 4.32, it is observed that the samples which required higher temperatures and toluene solvent to dissolve were the samples that underwent the least amount of degradation in terms of temperature and time, or no

70

degradation at all as in the case of our starting materials. Attempting to draw any concrete conclusions regarding which starting materials or conditions produce the most or the least branching could prove to be rather spurious due to the fact that there does not seem to be any solid trend. That aside, there are some general observations that can be made regarding the structure of the products and the experimental conditions under which they were produced. For the purposes of comparison the results include both of the starting materials (LLDPE and HDPE) as well a commercially available polyethylene wax (PW-725) which serves as a standard for our degradation products. In reviewing the data, one does note a trend where a large number of long chain branches are present, especially at higher temperatures. It appears that the higher temperatures promote an increased frequency of long chain branches versus short chain branches. As has been observed throughout the bulk of this work, the samples that most closely resemble the commercial wax were the polyethylenes degradaed in Parr reactor without catalyst. It appears as though using catalyst creates products that are highly branched, especially with isolated methyl and ethyl branches.

Table 4.14 Number of branch sites per 1000 methylene (-CH2-) units

|	Long branches	Isolated methyl branches	Methyl branches next to the chain end	Ethyl branches	Unsaturated bonds	Long chain ends
HDPE	0	0	0	0	0.5	0.3
LLDPE	0	0	0	18	0.1	1
PW-725	0.2	0	0	0	0	23
MD-PED-84-2 HDPE/415°C/2 hr	7	1	0	0	5	22
MD-PED-84-3 HDPE/415°C/4 hr	8	3	0	0	9	45
MD-PED-85-2 LLDPE/415°C/2 hr	7	1	0	13	6	28
MD-PED-85-3 LLDPE/415°C/4 hr	7	3	0	9	6	53
MD-PED-88 LLDPE/380°C/2 hr/Catalyst	2	3	1	18	1	3
MD-PED-90 LLDPE/415°C/1.5 hr/Catalyst	5	14	9	14	5	29
MD-PED-91 LLDPE/415°C/2 hr/Catalyst	4	14	11	11	5	30
MD-PED-94 HDPE/380°C/2 hr/Catalyst	1	3	1	1	2	3
MD-PED-96 HDPE/415°C/1.5 hr/Catalyst	4	10	5	3	4	18
MD-PED-97 HDPE/415°C/2 hr/Catalyst	3	13	8	4	4	28
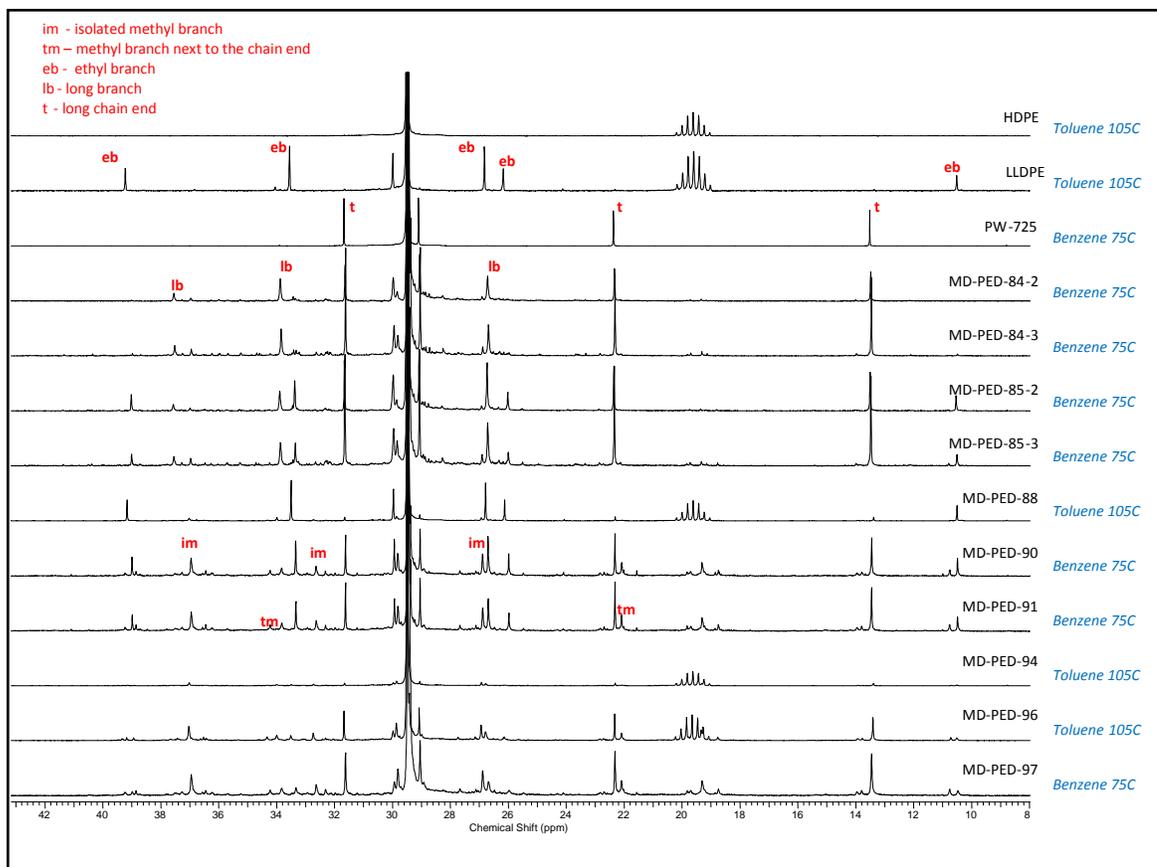
Figure 4.32 C-13 NMR plot showing branching in selected products of degradation

Chapter 5   Conclusions and Recommendations

5.1   Conclusions

The thermal degradation of linear polyethylenes (HDPE and LLDPE) was successful in producing a wax like material of reduced molecular weight. It was found that under similar conditions LLDPE generally degraded to a lower molecular weight than HDPE, however HDPE tended to produce a product which showed slightly better peak melting and sharper rheological properties.

The glass resin kettle under atmospheric conditions with nitrogen purge was effective in producing usable waxes with acceptable molecular weight. The resin kettle with catalyst was not as effective because the volatile components were continuously distilled off in large amounts before the polymer melt in the reactor could reach the desired molecular weight. The distillates captured in the receiver were very low molecular weight hydrocarbon liquids.

The Parr reactor which did not allow for the escape of volatiles had faster degradation times as compared to the resin kettle and produced materials that had acceptable molecular weight.

The silica-alumina catalyst used at a concentration of 5% caused very low molecular weight fractions to be produced quickly. Under atmospheric conditions these materials were distilled off as gasses and liquids. In pressure reactions the catalyst caused a rapid decrease in the molecular weight of the material which resulted in a significant accumulation of pressure as compared to pressure reactions without catalyst. For reactions that utilized catalyst, the added benefit of reduced time was offset by the

significant increase in the polydispersity of the degradation products both at atmospheric conditions and under pressure. Catalysts also increased the amount of branching in the final product as analyzed by NMR.

In summary, the molecular weight of the material produced was close to that of commercial waxes, and from this product, through distillation, a commercial narrowly distributed wax, as for example the wax reference utilized, could be produced.

5.2 Future Work

Future work that can be pursued in the area of degradation of linear polyethylenes;

•Model the degradation kinetics of the polymer melt.

•Combine the process developed here with a purification step such as short path distillation to purify the final product and obtain a low molecular weight distribution.

•Extend the work done here by examining how different catalysts and catalyst concentrations affect the products produced.

Nomenclature

D – Diameter (m)

DSC – Differential Scanning Calorimetry

HDPE – High Density Polyethyelene

HT-GPC – High Temperature Gel Permeation Chromatography

K_{pe} – Mark Houwink parameter for polyethylene

K_{ps} – Mark Houwink parameter for polystyrene

LLDPE – Linear Low Density Polyethylene

M_n – Number average molecular weight (g/mol)

Mp – Peak molecular weight

M_w – Weight average molecular weight (g/mol)

NMR – Nuclaer Magnetic Resonance Spectoscopy

PDI – Polydispersity index (Mw/Mn)

P_m – Polymer molecule of degree of polymerization m

P_n –Polymer molecule of degree of polymerization n

R – Radius

R_E – Radical of degree of polymerization n

R_j – Radical molecule of degree of polymerization j

RPM – Revolutions per minute (1/min)

Greek Letters

α – Mark Houwink Parameter

π – pi (3.14149)

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