ABSTRACT

PATTERSON, JOAN DIANA. Continuous Depolymerization of Poly(ethylene terephthalate) via Reactive Extrusion. (Under the direction of George Roberts and Saad Khan.)

A single-step, extrusion-based process to depolymerize poly(ethylene terephthalate) (PET) has been investigated. The depolymerization is effected by reacting ethylene glycol (EG) with the high molecular weight polymer (glycolysis). The ethylene glycol causes chain scission by attacking the ester linkages along the polymer backbone. The objective is to recover purified low molecular weight oligomers of bis(hydroxyethyl) terephthalate (BHET) for repolymerization. A key feature of this process is that it employs the use of a twin-screw extruder as a reactor. The twin-screw extruder conveys the polymer and continuously creates a fresh surface area that facilitates penetration of the depolymerizing agent into the polymer. This research could play a role in reducing the considerable amount of bottle-grade PET resin that is manufactured from virgin materials, resulting in a significant environmental and economic impact.

Results of glycolysis experiments on a Leistritz 34 mm counter-rotating twin-screw extruder have been characterized by substantially faster depolymerization rates than typical batch glycolysis reactions, shortening reaction times from hours to minutes. Oligomers with number-average degrees of polymerization (DPn) as low as 13 (Mn = 2,500) can be produced continuously from the starting bottle-grade PET resin (DPn = 102 and Mn = 20,000) in residence times of just 10 minutes. By changing operating conditions, e.g. feed rate and EG:PET ratio, the DPn of the final product can be controlled at essentially atmospheric pressure.
CONTINUOUS DEPOLYMERIZATION OF POLY(ETHYLENE TEREPTHALATE) VIA REACTIVE EXTRUSION

by

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DEDICATION

This work is dedicated to the most important people in my life: my family. Thanks to my mom Julia, my dad Bob, my sister Kristi and my brother Jack for all of their love, encouragement and support throughout my academic career.
BIOGRAPHY

Joan Diana Patterson was born on November 15, 1978 in Roanoke, VA. She grew up on a beautiful farm in Fincastle, VA where she lived with her parents, sister and brother. She attended Lord Botetourt High School in Daleville, VA and the Roanoke Valley Governor’s School for Science and Technology in Roanoke, VA. She graduated as valedictorian from Lord Botetourt in the spring of 1996. That same spring, she was awarded a Beneficial-Hodson scholarship to attend the Johns Hopkins University in the fall.

While at Johns Hopkins, she was an undergraduate assistant in the lab of Dr. Mark McHugh. She was chosen for an NSF internship at the IBM Almaden Research Center in San Jose, CA in the Summer of 1999. She graduated with honors in May 2000 with a B.S. in Chemical Engineering and a minor in Hispanic & Italian Studies.

After graduation, she decided to continue her education by pursuing a Ph.D. in Chemical Engineering. She accepted the offer to enroll at North Carolina State University and joined the department in August 2001. That fall, she chose a research project under the advisement of Dr. George Roberts and Dr. Saad Khan. In the Spring of 2002, she was named a National Science Foundation Graduate Research Fellow. In her time at North Carolina State, she was very active in the department, serving as a Graduate Student Association (GSA) officer and as a Recruiting Captain for the department. After graduation, she will pursue a career in industry.
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CHAPTER 1

PET RECYCLING

1.1 BACKGROUND

Since its discovery in the early 1940s, poly(ethylene terephthalate) (PET) has seen a fast rise in popularity among plastics. In the year 2000, world PET production capacity amounted to more than 66 billion pounds/year.\(^1\) While the largest end use of PET still goes toward making fibers, the second largest market is for bottle-grade resin. Production of bottle-grade PET worldwide exceeded 17.4 billion pounds/year in the year 2000. Demand for bottle-grade PET has grown steadily at 7-8% annually\(^2\).\(^3\) as applications broaden from water and soda bottles to beer, milk, wine and other specialty containers.\(^4\).\(^5\) As consumption of PET bottles continues to rise, the extent to which this plastic is recyclable becomes a key issue.

The first patents dealing with the chemical recycling of PET date back to the 1950s. PET is generally considered one of the easiest plastics to recycle. A typical 2-liter soft drink bottle consists of 1 g of polyethylene (PE), 5 g of label material (+ glue), and 60 g of PET, making the separation of components fairly straightforward (washing removes the glue and label while PE is separated from PET based on density differences). In fact, PET has one of the highest scrap values for recycled materials, second only to aluminum.\(^6\) However, when examining the recycled PET market for bottles in the United States, a discrepancy arises. According to the National Association for PET Container Resources (NAPCOR), 5.075
billion pounds of PET bottles were available in the U.S. for recycling in 2005. Of that amount, a mere 2.3% was recycled back into food and beverage containers. This clearly demonstrates the need for larger-scale recycling of PET into such high-value applications.

As described in guidelines put forth by the FDA, traditional PET recycling falls under three main categories. The primary means is an in-house recycling in which scrap PET from certain processes is redirected to other product lines. The secondary means is a physical reprocessing that involves washing, grinding, melting and reforming of post-consumer PET. It is by this means that the majority of PET is recycled, into sheet, fiber and strapping. The tertiary means is via a chemical recycling wherein PET is broken down into its originating monomers or oligomers which are then purified for repolymerization. Generally, in order to meet strict FDA regulations, processes for recycling PET for end-use in food or beverage containers must involve a chemical recycling step.

1.2 Research Introduction

This study investigates a single-step, extrusion-based process to depolymerize poly(ethylene terephthalate) (PET) and recover low-molecular-weight oligomers for repolymerization. A key feature of this process is that it employs the use of a twin-screw extruder as a reactor. The twin-screw can convey the polymer and continuously create a fresh surface area that facilitates penetration of the depolymerizing agent into the polymer. This research could play a role in reducing the considerable amount of bottle-grade PET resin that is
manufactured from virgin materials, resulting in a significant environmental and economic impact.

A review of scientific literature presented in Chapter 2 reveals that traditional depolymerization methods are far from ideal. They suffer from drawbacks including slow reaction rates, inability to run continuously and inefficiency in terms of yield and separation of depolymerization products. Furthermore, the kinetics and the equilibrium of the depolymerization reactions are not fully understood. In Chapter 3, we present a review of previous work dealing with the equilibrium of the PET polycondensation reaction, along with the results of our own experimental study on the equilibrium of melt glycolysis. In Chapter 4, we present a brief introduction to reactive extrusion as it applies to this research and discuss characterization of the twin-screw extruder as a reactor. In Chapter 5, we present the results of PET glycolysis in the twin-screw extruder and discuss the process parameters that affect the extent of depolymerization.

This project sought to address several issues in order to fully understand the reaction system. In particular, we sought answers to the following questions:

- What is the equilibrium constant for the melt glycolysis of PET?
- How does the extruder perform as a depolymerization reactor?
- What are the process parameters that influence the kinetics of this reaction?
- Can we use this knowledge to target a specific $\text{DP}_n$ of BHET oligomer as a product?
1.3 REFERENCES


2.1 INTRODUCTION

The chemical recycling of PET involves a partial to full depolymerization. The synthesis of PET is a reversible polycondensation. Therefore, addition of a condensation product to the polymer pushes the reaction in the reverse direction, favoring the formation of monomers and low-molecular-weight oligomers. Traditional depolymerization methods used for the chemical recycling of PET are hydrolysis, methanolysis and glycolysis wherein water, methanol and ethylene glycol, respectively, are the condensation products added to effect depolymerization.

In the hydrolysis reaction, shown in Figure 2.1, PET is reacted with water to produce terephthalic acid (TPA) and ethylene glycol (EG).

![Figure 2.1 Schematic of the PET hydrolysis reaction.](image-url)
By a similar mechanism, methanolysis involves reacting PET with methanol to yield dimethyl terephthalate (DMT) and EG (Figure 2.2).

The glycolysis reaction (Figure 2.3) results in the formation of bis(hydroxyethyl) terephthalate (BHET) and EG when PET is reacted with EG.
The reaction mechanism for PET depolymerization consists of three reversible reactions. The first step is a rapid protonation of the carbonyl carbon in the polymer chain wherein the carbonyl oxygen is converted to a second hydroxyl group. In the second step, the hydroxyl oxygen of the added hydroxyl-bearing molecule (i.e. water, methanol or ethylene glycol) slowly attacks the protonated carboxyl carbon atom. The last step is a rapid removal of the carbonyl oxygen (now a hydroxyl group) and a proton to form water or a simple alcohol and the catalytic proton. Because the second step is the slow step, the rate of depolymerization will vary based on how fast the depolymerizing agent can attack the carboxyl carbon after protonation.

Comparing the three depolymerizing agents, both methanol and ethylene glycol are weaker acids than water, with acid dissociation constant (pKₐ) values of 15.5 and 14.24, respectively, compared to a pKₐ for water of 14.0 (at 25°C). The order of nucleophilicity is inversely proportional to the strength of the acid, suggesting that of the three depolymerizing agents, water is the weakest nucleophile. Indeed, the hydrolysis reaction is slow in comparison to methanolysis and glycolysis. A further drawback to hydrolysis is that recovery of the TPA monomer typically requires many steps in order to reach the required purity. Depolymerization done via methanolysis also involves a costly separation and purification of monomers, rendering the process uneconomical. Glycolysis typically yields an end product that contains other higher oligomers in addition to BHET monomer, making it difficult to purify the product mixture if BHET monomer alone is desired.
A typical PET synthesis involves two steps and a schematic of the process is shown in Figure 2.4. In the first step, BHET oligomer is synthesized in an esterification reaction for use as a prepolymer in subsequent melt polymerization. The starting monomers can be either TPA and EG or DMT and EG, although due to increasing costs of DMT over TPA, PET synthesis using TPA has become almost the sole commercial means. The prepolymer made in the first step can have a degree of polymerization (DP) anywhere from 2-20. The second step is the melt condensation polymerization of the BHET oligomer (which regenerates EG) and yields a product with a DP around 80-100. The molecular weight of the product from step 2 can be increased further by adding an additional solid-state polymerization step to obtain PET with a DP anywhere from 100-145. This final step is necessary to produce a bottle-grade PET resin.

The objective of this project is to obtain a reaction product that can be repolymerized by conventional methods. Therefore, we will concentrate specifically on the glycolysis of PET, allowing production of BHET oligomers, or prepolymer, to be targeted directly. As shown in Figure 2.5, this product can be fed directly to the melt polymerization step for repolymerization, thereby producing a bottle-grade material from post-consumer materials.
2.2 HYDROLYSIS

Although hydrolysis is of less interest commercially due to long reaction times, high pressures and temperatures used and the high cost of purifying the reaction product, some of the earliest studies of PET depolymerization are in this area. Consequently, more in-depth analyses of this reaction have been carried out relative to methanolysis and glycolysis. Several kinetic studies have been done on hydrolysis of PET in the melt, the focus of this section, which better relate to reaction in an extruder than solution depolymerization. In the

**FIGURE 2.5** Schematic of PET production with recycling via glycolysis.
melt system, the PET is in a molten state and is in contact with water (or other condensation product being used to effect depolymerization). In a solution system, solid PET is suspended in the water (or other depolymerizing agent), typically in the form of pellets, chips, flakes, or powder.

Campanelli et al.\textsuperscript{8} authored one of the earliest kinetic studies of batch hydrolytic depolymerization of PET in the melt. Prior studies\textsuperscript{9, 10} by other researchers done at temperatures below the melting temperature of PET showed much lower reaction rate constants. Although lower rate constants would be expected at lower temperatures, Campanelli et al.\textsuperscript{8} speculated that the reaction at such conditions was also limited by mass transfer (diffusion of the depolymerizing agent into the polymer). To confirm, they used the Arrhenius equation to extrapolate values of the rate constant calculated from their work in the melt to such low temperatures as those used in solution hydrolysis. The rate constants they calculated in this manner were orders of magnitude \textit{greater} than those that were measured experimentally in the previous studies. This result supported the hypothesis that reaction rates in solution are dominated by mass transfer limitations and clearly demonstrated an advantage of performing hydrolysis in the melt-phase.

By varying the reaction temperature, Campanelli et al.\textsuperscript{8} concluded that the initial rate constant (i.e. the rate constant at short reaction times, less than 10 minutes) increased with increasing temperature. The extent of reaction decreased as the water:PET ratio was decreased. Values of the equilibrium constant were determined at 250°C, 265°C and 280°C.
This was done by charging the batch reactor with known quantities of reactants, allowing the reaction to reach equilibrium and analyzing the remaining amounts of reactant and product. The value of the equilibrium constant was very sensitive to temperature, dropping from 1.43 at 250°C to 0.384 at 280°C. This behavior suggests that the reaction is exothermic, although the heat of reaction is not mentioned. The activation energy for the hydrolysis was calculated to be 55.7 kJ/mol.

Campanelli et al.\textsuperscript{8} coupled the experimental studies on hydrolysis with an attempt to model the melt hydrolysis reaction. The rate equation for the appearance of carboxylic acid groups (corresponding to the product) was written as follows:

\[
\frac{dC_{\text{COOH}}}{dt} = k_{\text{EL}} C_{\text{WATER}} - k' C_{\text{COOH}} C_{\text{OH}}
\]  

(2.1)

where \(C_{\text{EL}}\) refers to the concentration of ester linkages in the polymer at any time, \(C_{\text{WATER}}\) the concentration of liquid water, \(C_{\text{COOH}}\) the concentration of carboxyl groups, and \(C_{\text{OH}}\) the concentration of hydroxyl groups (all concentrations in mol/g of PET). The symbols \(k\) and \(k'\) refer to the forward and reverse rate constants, respectively. The value of \(C_{\text{WATER}}\) was calculated using vapor-liquid equilibrium data and assuming that the only contributions to the reactor pressure were due to saturated water vapor and air. This value was assumed to be constant throughout the reaction due to the large excess of water used. Campanelli et al., neglecting the reverse reaction, obtained a good fit of the experimental data to Equation (2.2) at short times (less than 10 minutes) for the excess water condition where pseudo first-order
kinetics were assumed. The subscript \( \text{subscript}_0 \) in the equation signifies the initial concentration at time \( t = 0 \).

\[
\ln\left[\frac{C_{\text{COOH}} - C_{\text{COOH}_0}}{C_{\text{ELo}} - C_{\text{COOH}_0}}\right] = (kC_{\text{WATER}}) \cdot t \tag{2.2}
\]

A later study by Kao et al.\(^{11}\) found that the conversions of PET melt hydrolysis reached high values, close to complete depolymerization, even at reaction times of just 10 minutes at 265°C. This suggests that the concentration of the products in the system was considerable even at short times and therefore no longer negligible. The researchers concluded that the reverse reaction had to be considered in the rate equation regardless of reaction time. Campanelli et al.\(^{8}\) concurred that the reverse reaction would ultimately determine the equilibrium in the complete hydrolysis reaction, and derived the following model (in final form) for the melt hydrolysis using Equation (2.1) as a starting point:

\[
\ln\left[\frac{C_{\text{COOH}} + A - B}{C_{\text{COOH}} + A + B}\right] = -2B(k' - k)t + \ln\left[\frac{C_{\text{COOH}_0} + A - B}{C_{\text{COOH}_0} + A + B}\right] \tag{2.3}
\]

where,

\[
A = \frac{k(C_{\text{ELo}} + C_{\text{WATER}})}{2(k' - k)} \tag{2.4}
\]

\[
B = \left(\frac{k^2(C_{\text{ELo}} + C_{\text{WATER}})^2}{4(k' - k)^2} + \frac{kC_{\text{ELo}}C_{\text{WATER}}}{k' - k}\right)^{1/2} \tag{2.5}
\]
This model provided good agreement with their experimental results (obtained at 265°C for reaction times up to one hour) and was also fairly successful at providing an estimate of the equilibrium carboxyl group concentration. They found effectively complete hydrolysis at a water:PET ratio of 5:1 (w/w) or greater with a reaction time of at least 60 minutes. At charge ratios below that amount, the reaction reached equilibrium before complete conversion was attained.

In an additional study, Campanelli et. al\textsuperscript{12} investigated the influence of addition of catalysts on the rate of melt hydrolysis. Both zinc stearate and zinc acetate were studied at concentrations equal to or greater than 1.58 x 10\textsuperscript{-3} mmol Zn\textsuperscript{2+}/g PET. They found that the addition of catalyst resulted in a modest increase of the reaction rate, with values of the rate constant that were 20% greater than their previous results for the same system.

Kao et al.\textsuperscript{11} investigated several reaction parameters in the melt system that Campanelli’s group did not, including a study of the influence of mass transfer in the system. This was done by determining the effect of agitation speed (varied between 50-600 rpm) on the extent of the PET hydrolysis after 10 minutes at 250°C. It was found that at agitation rates below 400 rpm, the reaction extent increased with the agitation speed. Above 400 rpm, there was no variation, indicating that there was a mass transfer limitation that could be removed at high agitation rates. This could be one reason that Kao’s reaction times are so much lower than Campanelli’s for the same system, as Campanelli makes no mention of the agitation speed in the reactor.
Kao also examined the effect of using different PET resins on the extent of reaction. The results showed minimal difference between fresh PET chips and recycled flakes if both were clear (IV=0.54 and 0.80 dl/g, respectively). However, recycled flakes that were green (IV=0.70 dl/g) showed lower extents of reaction. This indicated that the shape and molecular weight of the PET resin did not influence the hydrolytic reaction in the melt state at high temperature, but that perhaps additives in the green PET affected the conversion.

There is one study of hydrolytic depolymerization in an extruder performed by Yalçinyuva et al.\textsuperscript{13} that relates closely to this work. Although this research will be reviewed in more depth in Chapter 5, the researchers report that oligomers with an average $M_n$ of 325 (essentially complete hydrolysis) were produced at 4757 kN/m$^2$ (about 700 psi), their highest operating pressure, 300$^\circ$C, their highest operating temperature, and a residence time of about 3 minutes.

2.3 METHANOLYSIS

As mentioned previously, traditional depolymerization products of PET methanolysis are DMT and EG. Because almost all current PET production facilities use a TPA-based synthesis, the methanolysis of PET has become obsolete due to lack of usefulness of recovering the DMT monomer. Consequently, the literature does not contain many detailed analyses of the kinetics of the methanolysis reaction. Although methanolysis has been modeled only as pseudo first-order in methanol and for short times, what is more interesting
for these reactions are the parameters investigated by different groups. In their studies of methanolysis, Goto et al.\textsuperscript{14, 15} used a batch reactor operated at high temperatures and pressures (573-623K and 20MPa) at which methanol is in the supercritical state and PET is in a molten state. They found that higher temperatures increased the initial rates of reaction but at longer times, operation at higher temperatures increased the yield of products from undesired side reactions. This brought into question the ease of separation of the desired product.

Another study of supercritical methanolysis (at temperatures from 523-543 K where PET is in a molten state and pressures from 8.5-14.0 MPa) in a batch reactor by Yang et al.\textsuperscript{16} interestingly revealed that increasing the temperature increased the rate of the reaction at short times but that in order to approach 100\% conversion, the reaction still had to proceed for at least 40 minutes at any temperature. Above the critical pressure of methanol, no influence of any further increase in pressure on the depolymerization degree was observed. This group also investigated different sources of PET including green and transparent bottles and waste fiber and found no significant difference in the degree of PET depolymerization among them, reaching greater than 96\% depolymerization for each source.

2.4 Glycolysis

Research on the glycolysis of PET in the literature dates back to 1960 and involves early efforts to understand the polycondensation equilibrium in presence of the reverse reaction.
These efforts were undertaken primarily by Challa\textsuperscript{17-19} and were followed up on by Stevenson and Nettleton\textsuperscript{20} and Fontana.\textsuperscript{21} Although these works deserve mention here, they are not targeted at recovering BHET or oligomers and contain only a brief mention of the kinetics of the reverse reaction. They will be covered in more detail in Chapter 3 with a discussion of the equilibrium of melt glycolysis. In this section, we will review glycolysis studies in the scientific literature aimed at depolymerization and select works from patent literature that have high relevance.

2.4.1 Batch Glycolysis

Of the studies that investigate the glycolysis of PET, the majority are carried out using batch reactors. There are 2 distinct systems; those that employ temperatures below the melting point of PET and at or above the boiling point of EG, or solution glycolysis, and those that investigate the glycolysis of PET in the melt, or melt glycolysis.

Solution glycolysis is carried out at temperatures ranging from 190°C-245°C. In such systems, PET flakes, typically, are suspended in medium of ethylene glycol alone or mixed with another solvent, creating a two-phase reaction system. Once the reaction reaches a high conversion, the low-molecular weight oligomers (DP=2-4) are soluble in the heated ethylene glycol. Typical reaction times in these systems range from 60-90 minutes or longer to achieve high conversions.
Studies on solution glycolysis date from the 1980s, although there are patents that deal with this type of glycolysis dating from the 1970s. From 1987-1989, Vaidya and Nadkarni\textsuperscript{22-24} published several works dealing with the synthesis of polyester polyols from PET waste. In order to obtain starting materials with which to conduct the synthesis, they first depolymerized waste PET using propylene glycol and ethylene glycol. In their studies, they conducted the glycolysis reaction at 200°C for 8 hours using large excesses of PG/EG (up to 62.5:37.5 EG:PET by weight) in the presence of a zinc acetate catalyst. They were able achieve nearly complete depolymerization to BHET monomer under these conditions. In 1989, Baliga and Wong\textsuperscript{25} published a study on the glycolysis of post-consumer PET bottle chips. They observed that equilibrium between the BHET monomer and dimer was reached after allowing the system to react for 8 hours at 190°C with an excess of EG, also in the presence of a metal acetate catalyst. At equilibrium, they found that only 25\% of the initial EG was consumed from an initial EG:PET weight ratio of 43.8:56.2. By testing zinc, lead, manganese and cobalt acetates they concluded that the type of catalyst affected the initial rate of the reaction but not the final equilibrium attained. When testing the glycolysis of green bottle chips, they saw no difference in the extent of depolymerization as compared to clear chips.

In the 1990s, more studies using batch reactors in the same temperature range were conducted. Researchers were able to get reaction times down from 8 hours to 2-3 hours for the same extents of conversion.\textsuperscript{26-28} Chen et al.\textsuperscript{26} found that without catalyst in the system, PET flakes still remained in the system even after 10 hours. With the addition of catalyst,
however, the PET flakes disappeared after 2 hours and the reaction mixture became one-phase.

There has been a large increase in the number of glycolysis studies since the year 2000. In general, these works have searched for optimum conditions under which to carry out the reaction, investigating variables such as temperature, reaction time, particle size, and reaction catalyst.

Chen\textsuperscript{29} studied the glycolysis of post-consumer PET soft-drink bottles at 190\textdegree C and found that the optimal reaction conditions for producing predominantly BHET monomer and dimer were reaction times of 1.5 hours using manganese acetate as a catalyst. Xi et al.\textsuperscript{30} studied the glycolysis of PET waste bottles at 196\textdegree C. In order to obtain 85.6\% yield of BHET, their optimal operating conditions were reaction times of 3 hours in the presence of zinc acetate catalyst. Mishra and Goje\textsuperscript{31, 32} investigated the glycolysis of PET scrap at 197\textdegree C and found optimal reaction times of 90 minutes for close to 99\% PET conversion, using zinc acetate catalyst.

Other groups investigated the effect of using non-traditional catalysts in the reaction system. Shukla and Kulkarni\textsuperscript{33} found that qualitative and quantitative yields of BHET monomer using alkali catalysts for the glycolysis reaction were equivalent to those obtained using conventional heavy metal catalysts like zinc and lead acetates, which are known to have detrimental effects on the environment. Troev et al.\textsuperscript{34} replaced the traditional zinc acetate
catalyst with a novel titanium (IV)-phosphate catalyst. They saw improvement of reaction rates using the titanium (IV)-phosphate catalyst when depolymerizing fiber-grade PET (M_w = 30,000), but no distinction between the two when depolymerizing bottle-grade PET (M_w = 51,000).

Still other groups performed glycolysis of PET in order to collect the depolymerization products for use in other applications. Grzebieniak and Wesolowski^35 recovered oligomers to use in the synthesis of co-polyesters of ethylene terephthalate and L-lactic acid. Pimpan et al.^36 and Öztürk and Güçlü^37 were both interested in using glycolyzed products to synthesize unsaturated polyester resins.

Although some researchers were pushing for new advancements in the field, still others were stuck at the same old conclusions. For example, in a 2005 study on batch glycolysis of PET fibers in solution,^38 the research team concluded that a minimum reaction time of 8 hours was needed to achieve a conversion close to 85%.

One interesting feature of the publication by Mishra and Goje^31 is that they address mass transfer effects in the system by studying the influence of particle size on the glycolysis rate. PET waste powder was used with particle sizes ranging from 50 to 512 µm. At particle sizes smaller than 150 µm, there was no effect on the glycolysis rate or rate constant. Beyond 150 µm, the rates dropped substantially with an increase in particle size. This result indicates that diffusion into the pellet is important and can limit the reaction for large particle sizes.
Mass transfer concerns are not eliminated entirely when moving to a melt system. Campanelli et al.\textsuperscript{39} conducted the only literature study of glycolysis of PET in the melt state, published in 1994. Using a batch reactor at temperatures above 245°C, they performed glycolysis experiments at reaction times up to 11 minutes, reaching conversions close to 50%. The rate constants they calculate for the initial reaction rate are similar to those found by other researchers using a two-phase system. They claim that the reactor is equipped with rotors to ensure proper mixing but do not mention the agitation rate, shown to be important in a melt system by Kao et al.\textsuperscript{11} in their studies on PET hydrolysis. While Campanelli’s study of melt hydrolysis\textsuperscript{8} was thorough enough to show advantages over solution hydrolysis, this study does not tackle that issue. They do, however, present a kinetic model for the system. While the reverse reaction is neglected in their analysis, pseudo first-order kinetics are not assumed in the following model for glycolysis:

\[
\frac{d[EG]}{dt} = -\frac{d[EDE]}{dt} = k_G [EG][EDE]
\]

(2.6)

where [EG] is the concentration of ethylene glycol, [EDE] is the concentration of ethylene diester groups and \(k_G\) is the glycolysis rate constant. Although Challa\textsuperscript{17} originally found the glycolysis rate to have a linear dependence on the EG concentration, it has since been proposed that the glycolysis reaction may see some auto-catalytic effect by ethylene glycol in the system.\textsuperscript{27} This would make the rate equation second-order in [EG], but Campanelli shows
that better fits to literature data are obtained using an equation that is first-order in \([\text{EG}]\), shown in Equation (2.6).

Thus, by writing a component balance for liquid EG and stoichiometrically relating the amount of EG reacted to the amount of EDE groups remaining in the PET, the following equation can be found:

\[
-d[\text{EDE}] \frac{dt}{dt} = k_c [\text{EDE}][[\text{EDE}]+A)
\]

(2.7)

where the constant A is defined as \(A = [\text{EG}]_0 - [\text{EDE}]_0\), and the subscript 0 refers to the concentration that is initially present in the system at time zero. Solution of Equation (2.7) with integration limits of 0 and \(t\) for time and \([\text{EDE}]_0\) and \([\text{EDE}]\) for concentration of EDE groups yields the following:

\[
\frac{1}{A} \ln \frac{1}{(1-X)} = k_c t
\]

(2.8)

\[
X = \frac{A([\text{EDE}]_0 - [\text{EDE}])}{[\text{EDE}]_0([\text{EDE}] + A)}
\]

(2.9)

where \(X\) represents the fractional conversion of \([\text{EDE}]\) groups and varies between 0 and 1. All concentrations here are in mol/L. Using Equation (2.8), Campanelli obtains excellent fits to experimental data at temperatures of 255°C, 265°C and 275°C, but only for reaction times...
of up to 11 minutes (reaction extents below 50%). Data is not presented for longer reaction times and therefore the applicability of the model to complete glycolysis or even close approaches to equilibrium is not confirmed.

2.4.2 Continuous Glycolysis

Patent literature reveals a few processes for continuous glycolysis of PET. The earliest work was done by Ostrowski\textsuperscript{40} in 1970. He presents a process for depolymerizing PET into low-molecular-weight oligomers in a continuous stirred-tank reactor (CSTR). In this system, he reports residence times of 1.5-2 hours at 230\degree C, obtaining BHET oligomers with an average DP of 2-4. Malik et al.\textsuperscript{41} followed that work with a patent covering a glycolysis process operated at temperatures between 225\degree C-235\degree C. While they claim that the process is operated continuously, they describe hold-up times (where hold-up time is defined as the time elapsed from the time EG is added to the reactor to the time glycolysis is complete) of 4 hours to 15 hours. Finally, in 2 separate patents, Ekart et al.\textsuperscript{42,43} present a continuous process for glycolysis in a stirred reactor. They operate at 180\degree C-240\degree C for reaction times up to 4 hours in order to produce an “oligomeric material” that is fed to a downstream process for separation of impurities.

Recently, Colomines et al.\textsuperscript{44} reported the use of a twin-screw extruder for glycolysis of PET via oligoester diols to study polyurethane formulations. Compared to their own work studying the batch formation of such glycosylates,\textsuperscript{45} Colomines et al. saw batch reaction
times of 2 hours drop to extruder residence times of 2-4 minutes, demonstrating the advantage of using a continuous reactor for such processes.

Although the depolymerization of PET was introduced merely a decade after PET itself, the depolymerization processes that have been developed to date are far from ideal. The need to develop an efficient and economical process for the glycolysis of PET is evident, and the motivation for this work investigating a single-step extrusion-based depolymerization of PET is clear.

2.5 References


CHAPTER 3

THE EQUILIBRIUM OF PET MELT GLYCOLYSIS

3.1 INTRODUCTION

The glycolysis of PET is effected by reacting the polymer with ethylene glycol. The ethylene glycol attacks the ester linkages along the PET backbone, causing chain scission and resulting in the production of low-molecular-weight oligomers. The glycolysis reaction is reversible and therefore requires an understanding the equilibrium of the system so that the desired conversion and reaction products in the chemical recycling process can be obtained.

In order to recover oligomers of BHET of a specific DP and not just the monomer, a large excess of EG cannot simply be fed to the system as has typically been done in previous glycolysis research. Producing an oligomer requires knowledge of not only the stoichiometric amount of EG needed to reach a certain DP but also the additional amount of EG that is required to hold the system at equilibrium at that point and prevent the reaction from reversing. In order to determine that quantity of EG, the equilibrium constant for the depolymerization reaction must be known. In the literature, the value of the equilibrium constant for polycondensation has been studied in detail because of its importance in PET synthesis. The polycondensation reaction is considered the forward reaction, with equilibrium constant $K_{eq}$. The reverse reaction is the depolymerization reaction and in order to distinguish the two, the equilibrium constant for depolymerization will be referred to as
$K_{dep}$. The relationship between the equilibrium constants for the forward and reverse reactions is as follows:

$$K_{dep} = \frac{1}{K_{eq}}$$  

3.2 POLYCONDENSATION EQUILIBRIUM

Most step-growth polymerizations are reversible. For these systems, it is important to know the conversion and the molecular weight distribution of the polymer at equilibrium. For polyesterification reactions (forward), the equilibrium constant, $K_{eq}$, is typically in the range of 1-10 and for transesterifications (forward), the value drops to 0.1-1.\(^1\) It is expected that the value of the equilibrium constant for PET polycondensation, $K_{eq}$, will fall in this range and consequently, the value of the equilibrium constant for depolymerization, $K_{dep}$, will be on the order of 1.

As mentioned in Chapter 2, studies on the equilibrium of melt polycondensation of PET were pioneered by Challa\(^2-4\) in 1960. He looked at the equilibrium reached between BHET monomer, dimer and higher oligomers at temperatures over a range of 195°C-282°C in the absence of catalyst. For samples with an average DP\(_n=1.05\) at temperatures of 254°C, the equilibrium constant is 0.47. As the DP\(_n\) of the sample increased, the value of the equilibrium constant increased. For an average DP\(_n = 2.22\), $K_{eq} = 0.73$ at 254°C. For DP\(_n = 3.02\), $K_{eq} = 0.87$ at 262°C while for a DP\(_n = 33\), $K_{eq} = 1.1$ at 262°C. Using Challa’s range of
values, we can estimate the value of $K_{dep}$ to be in the range of 2.6-0.9 at temperatures between 254°C-282°C.

Challa concludes that while the value of $K_{eq}$ increases greatly with increasing extent of polymerization (demonstrated at 262°C), the effect of temperature on $K_{eq}$ is minimal. For the DP$_n = 1.05$ sample, Challa measured the equilibrium constant at four temperatures: 195°C, 223°C, 254°C and 282°C. As the temperature increased, the value of the equilibrium constant for polycondensation, $K_{eq}$, dropped from 0.59 to 0.51, 0.47 and 0.38, respectively. While the difference in values is not large, it does indicate that increasing the temperature causes a decrease in the value of $K_{eq}$. This is expected behavior for an exothermic reaction and in fact, most step polymerizations are exothermic. For the polymerization reaction of TPA with EG, used to make BHET oligomers, the heat of reaction, $\Delta H_R$, is -10.9 kJ.mol.$^1$

For an endothermic reaction, the value of the equilibrium constant should increase with increasing temperature. Kao et al.$^5$ monitored the glycolysis reaction by differential scanning calorimetry (DSC). Their results show a reaction endotherm, i.e. a positive heat of reaction, for glycolysis. A value of $\Delta H_R$ for PET glycolysis can be estimated by finding the difference in activation energy ($E_a$) between the polycondensation and glycolysis reactions. For the transesterification of BHET, the typical value of $E_a$ is 188 kJ/mol in the absence of catalyst.$^1$ The value of $E_a$ for glycolysis is fairly consistent in the literature and is reported to be 92 kJ/mol, but this value is calculated in the presence of catalyst.$^2$, $^3$, $^6$, $^7$ Therefore, we estimate
that $\Delta H_R$ for glycolysis is the opposite of that for the transesterification of TPA and EG, about +10.9 kJ/mol.

Stevenson and Nettleton$^8$ followed Challa’s work with a study of melt polycondensation equilibrium in the presence of an antimony trioxide catalyst. They report that the equilibrium constant, $K_{eq}$, for a range of temperatures from 231-251°C is 0.36 with no discernible influence of temperature. At the same time, Fontana$^9$ published a study of the polycondensation equilibrium in the presence of lead, zinc and calcium salts over a temperature range of 199°C-278.5°C. He found an average value of $K_{eq}$ of 0.5.

Baliga and Wong,$^{10}$ in their study of PET depolymerization via glycolysis at 190°C, report values of 1.13-1.53 for the equilibrium constant between 2 BHET molecules, a dimer and EG. Collectively, these values suggest that the equilibrium constant for glycolysis should be on the order of 1, but there remains ambiguity about where it falls exactly. For this reason, we found it essential to conduct our own study on the equilibrium of PET glycolysis in the melt.
3.3 Experimental Procedure

3.3.1 Materials

Bottle-grade (CB12) virgin PET resin used in this study was donated by Voridian (M_w = 55,000; PDI = 2.8; IV=0.83). Ethylene glycol (purity > 99%) from Acros Organics was used as received.

3.3.2 Method

Reactions were carried out in 5 mL stainless steel Micro-reactors from High Pressure Equipment. The reactors were immersed in a Fisher High-Temperature Bath filled with Dynalene 600 heat transfer fluid, stable to 288°C. Reactors were stabilized on a platform which oscillated up and down within the bath, while stainless steel balls were added to the reaction mixture to ensure proper agitation. Reactions were run at 260°C with varying EG:PET charge ratios from 0.5 to 1. Reactors were left in the bath for times of up to 6 hours to ensure the reaction had reached equilibrium. The reactions were quenched immediately upon removal from the oil bath by immersing the reactors in cold water. Reaction products were collected from the reactors and dried in a vacuum oven for at least 12 hours at 90-100°C to remove EG. A detailed description of the procedure including product analysis can be found in Appendix A.1.
3.3.3 Product Analysis

The products were analyzed using a hydroxyl end group titration. The procedure for the hydroxyl end group titration was taken from ASTM D2849 Method A, described by Chen et al.,\textsuperscript{11} with the exception that dry dichloroethane was used instead of benzene according to the procedure described by Polk.\textsuperscript{12} A summary of the method used is as follows. Between 0.35 – 0.50 g of sample was weighed into a 100-mL reaction flask and 10 mL of the acetylation solution (1.2 mL of anhydrous pyridine and 8.8 mL of acetic anhydride) was added. The flask was fitted with a reflux condenser and heated in a boiling water bath under stirring until the polyol sample was completely dissolved. After complete dissolution, the flask was removed from the water bath and 10 mL of dry dichloroethane was added under stirring. Next, 100 mL of water was added to the mixture under stirring and the solution was titrated with 0.5 N KOH solution, using phenolphthalein as an indicator. A blank run without the sample was also performed.

The hydroxyl value is calculated from the following equation

\[
\text{Hydroxyl value} = \frac{56(v_1 - v_2)n}{m}
\]

(3.2)
where \( v_1 \) and \( v_2 \) are the volumes in mL of 0.5 N KOH used for titration of the blank and the sample, respectively; \( n \) is the normality of the KOH solution, and \( m \) is the weight of the polyol sample in grams.

The hydroxyl value can be used to calculate the average degree of polymerization (DP\(_a\)) of the product which is then used to calculate the value of the equilibrium constant for depolymerization, \( K_{dep} \). A sample calculation can be found in Appendix A.2.

### 3.4 Results and Discussion

We follow the reverse reaction by monitoring the concentration of functional groups in the system, as described by Challa.\(^4\) The balanced equation describing the glycolysis of PET is below:

\[
\text{PET} + (n-1) \text{EG} \leftrightarrow n \text{BHET} \quad (3.3)
\]

When written in terms of functional groups, this equation becomes:

\[
\text{EDE} + \text{EG} \leftrightarrow 2 \text{HEE} \quad (3.4)
\]
where HEE is the hydroxyl ethyl ester group in BHET, EDE is ethylene diester group in the PET backbone, and EG is ethylene glycol.

The equilibrium constant of this reaction can thus be written in terms of functional groups as:

$$K_{dep} = \frac{[HEE]^2}{[EDE][EG]}$$

(3.5)

The quantities of each are in molar equivalents per mole repeat unit. The values of [HEE], [EDE] and [EG] can be written in terms of DP, allowing Eq. (3) to be solved using the average DP, calculated from the hydroxyl number. For our calculations of $K_{dep}$, we assume that all of the EG charged to the reactor remains in the liquid phase.

Following are the results of equilibrium experiments run at 260°C for varying EG:PET ratios. Figure 3.1 shows the progression of the glycolysis reaction over time for an initial EG:PET charge of 1:1 (w/w). From the data points at short times, we can see that the reaction reaches equilibrium quickly, i.e. in about 1 hour. This is supported by work done by Chen et al., who also show that this reaction proceeds to a mixture of trimer, dimer and monomer within 1.5 hours, after which equilibrium is reached among those 3 species. As shown in Figure 3.1, we found the average OH# for this reaction to be 340, corresponding to an average DP, of 1.74, which supports the findings of Chen.
Figures 3.2 and 3.3 show results for the EG:PET = 0.67:1 and EG:PET = 0.05:1 cases, respectively, with values of the average OH# and DPn shown.

**Figure 3.1** Batch glycolysis of PET at 260°C, EG:PET=1:1 (w/w).

**Figure 3.2** Batch glycolysis of PET at 260°C, EG:PET=0.67:1 (w/w).
Values of the equilibrium constant for glycolysis, $K_{dep}$, for each EG:PET ratio are shown below in Table 3.1. The error shown is the standard deviation in the value of $K_{dep}$ calculated for each data point obtained at equilibrium.

**Table 3.1** Equilibrium constant, $K_{dep}$, at varying EG:PET ratios (w/w) and temperatures.

<table>
<thead>
<tr>
<th>EG:PET (w/w)</th>
<th>Temperature (°C)</th>
<th>OH$_{eq}$</th>
<th>DP$_{eq}$</th>
<th>$K_{dep}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>260</td>
<td>248</td>
<td>2.37</td>
<td>1.1 ± 0.4</td>
</tr>
<tr>
<td>0.67</td>
<td>260</td>
<td>276</td>
<td>2.13</td>
<td>1.1 ± 0.3</td>
</tr>
<tr>
<td>1:1</td>
<td>260</td>
<td>340</td>
<td>1.74</td>
<td>1.2 ± 0.3</td>
</tr>
<tr>
<td>1:1</td>
<td>270</td>
<td>306</td>
<td>1.91</td>
<td>0.8 ± 0.2</td>
</tr>
</tbody>
</table>
Based on these results, there does not seem to be any influence of the charge EG:PET ratio, or the extent of depolymerization, on the equilibrium constant. This contradicts what Challa found in his studies of polycondensation equilibrium, although in our reactions, the values of the average DP$_n$ for each ratio are very close to one another, varying only from 1.74 to 2.37 while those of Challa ranged from 1.05 to 33.

We also investigated the influence of temperature by conducting equilibrium reactions at 270°C for an EG:PET ratio of 1:1 (w/w). The reactions were allowed to proceed for up to 6 hours with the results shown in Table 3.1. Although the value of 0.8 for $K_{dep}$ at 270°C is slightly lower than those measured at 260°C, it does not fall outside of experimental error and therefore is not significantly different. This is consistent with early works that concluded that temperature had little influence on the equilibrium of the polycondensation reaction, but it is not expected behavior for an endothermic reaction.

It is also possible to predict the average DP$_n$ that can be obtained at equilibrium by modeling the depolymerization kinetics. The glycolysis reaction can be written as follows, assuming the reaction only takes place in the liquid phase and that there is no monomer or polymer in the vapor phase:

$$\frac{d}{dt}(V_L P_i) = V_L \left\{-k_f P_i (i-1)C_E + k_b \sum_{j=1}^{i-1} P_j P_{i-j} + 2k_f \sum_{j=i+1}^{\infty} P_j C_E - 2k_b \sum_{j=i+1}^{\infty} P_i P_{j-i}\right\}$$  (3.6)
where $C_E$ is the molar concentration of EG in the liquid phase, $P_i$ is the molar concentration of polymer with DP = $i$, $V_L$ is the volume of the reactor, $k_f$ is the rate constant for depolymerization in the forward direction and $k_b$ is the rate constant for the backward reaction (i.e. $K_{dep}$ is defined as $k_f/k_b$). By using a generating function, $G$, and taking the limit of $G$ as $s$ goes to 1, the following expression is derived (the derivation of Equation 3.7 can be found in Appendix A.3):

$$\frac{1}{V_L} \frac{d}{dt} (V_L \mu_0) = k_f C_E (\mu_i - \mu_0) - k_b \mu_0^2$$

(3.7)

At equilibrium, $d\mu/dt = 0$, and therefore the following expression for the equilibrium constant for depolymerization, $K_{dep}$, is found:

$$K_{dep} = \frac{\mu_0^3}{C_E (\mu_i - \mu_0)}$$

(3.8)

Now, the depolymerization can also be written as follows:

$$[A - A]_{m} + C_E \leftrightarrow [A - A]_n + [A - A]_m$$

(3.9)

In this representation, BHET, for example, can be thought of as a chain with one repeat unit, i.e. $n = 1$, and two identical end-groups, or as $[A-A]_L$. Writing an expression for equilibrium assuming that BHET is one of the depolymerization products (i.e. that depolymerization is
complete or nearly complete) leads to the following equation (the derivation of Equation 3.10 can be found in Appendix A.4):

\[
\frac{[A - A]_m}{[A - A]_1} = \alpha^{n-1}
\]  

(3.10)

where

\[
\alpha = \frac{1}{K_{dep}} \frac{[A - A]_1}{C_E}
\]  

(3.11)

The value of the first moment, \( \mu_1 \), is known for the starting high- molecular-weight PET and can be written as:

\[
\mu_1 = \sum_{1}^{\infty} n [A - A]_n
\]  

(3.12)

Substituting Equation (3.9) into Equation (3.10), an expression for \( \mu_1 \) in terms of \([A-A]_1\) can be found:

\[
\mu_1 = [A - A]_1 \frac{1}{(1 - \alpha)^2}
\]  

(3.13)

Similarly,
\[
\mu_0 = [A - A]_1 \frac{1}{(1 - \alpha)}
\]  

(3.14)

By estimating the solubility of EG in PET and assuming that the value of \( K_{\text{dep}} \) is 1.0, the value of \([A - A]_1\) can be found. With this value, full distribution of oligomers can be calculated. Figure 3.4 shows the predicted distribution of oligomers at equilibrium at 260°C, using a 1 kg basis for the initial amount of PET, or \( \mu_1 \), and assuming that the solubility of EG in PET or oligomers is the same as the solubility of EG in BHET monomer (solubility estimated using ASPEN, see Appendix A.5 for more details).

The value of \( \text{DP}_n \), or \( \mu_1/\mu_0 \), from this prediction is 3.12. This value is close to the experimental values of \( \text{DP}_n \) that were calculated from the hydroxyl end-group titrations for nearly complete glycolysis.
3.5 Conclusions

From the experimental data, we can see that the extent of depolymerization in all three cases is substantial, with average DP\textsubscript{n} values ranging from 1.74-2.37, suggesting a mixture of low-molecular-weight oligomers. The batch reaction appears to reach equilibrium very quickly, in less than 1 hour.

For each set of EG:PET ratios, the equilibrium constant was found to be very close to 1. This falls within the expected range based on literature values given for the polycondensation equilibrium constant. However, we have been able to measure values of the equilibrium constant for glycolysis directly, furthermore relevant to this work in that they are for melt systems at the operating temperatures used in the extruder.

Additionally, we have modeled the reversible depolymerization and have been able to predict the distribution of oligomers that would be present at equilibrium. This further illustrates that the calculated value of DP\textsubscript{n} for the reaction products is an average value.

3.6 References


CHAPTER 4

EXTRUDER CHARACTERIZATION

4.1 INTRODUCTION

Extruders are used for a number of reactive processes because they offer several inherent advantages over other reactors. It is important to be familiar with the reaction process needs before selecting the reaction equipment, but extruders have become commonplace because they provide an environment with consistently high levels of dispersive and distributive mixing, good temperature and residence time distribution control, the ability to run continuously, under pressure and with different stages, and relative ease of melt feed preparation and unreacted monomer/by-product separation. Their limitations are few but include an inability to handle large heats of reaction.

In the plastics industry, twin-screw extruders have emerged as the primary reaction vessel because they offer improved mixing, larger heat transfer, larger melting and devolatilization capacity and better temperature control over single-screw extruders. Moreover, since the screws are modular, mixing or conveying elements can be configured toward a specific process. One disadvantage is that the flow and velocity profiles in a twin-screw extruder are much more complicated and prediction of performance is difficult because the theory is not as well-developed as for single-screw extruders.
Extruders are now used for a wide variety of reactions including bulk polymerizations, condensation polymerizations, addition polymerizations, graft reactions, copolymer formation, crosslinking reactions, controlled degradation, and functional group modification.\textsuperscript{2} Controlled degradation of polymers involves lowering the molecular weight of the polymer to a desired point, i.e., depolymerization. The greatest amount of research has been done on the depolymerization of polypropylene and other polyolefins, but polyesters, polyamides and biological polymers have also been studied.

4.2 **Twin-screw Extrusion System**

The heart of this research is the extrusion system that is shown in Figure 4.1.

![Figure 4.1 Schematic of Twin-screw Extrusion System.](image)

**Figure 4.1** Schematic of Twin-screw Extrusion System.
The main component in this system is a Leistritz 34mm (LSM 34-GG) fully intermeshing counter-rotating twin-screw extruder (TSE). There is a feed section followed by 12 barrel sections including the extruder die and the L/D is about 42/1. Attached to the TSE is a Randcastle 1” single-screw Microtruder, in series. The polymer is first fed through the single-screw extruder (SSE), whose barrel length is used to ensure that the polymer is fully molten before feeding into the TSE. The screw configuration of the TSE is such that a melt seal is formed at the feed end. At zone 2, after the melt seal, the extruder is configured with 2 injection ports. The first port is configured for the injection of supercritical carbon dioxide, while the second port is configured for ethylene glycol injection. These are fed to the system using ISCO 260-D continuous-flow syringe pumps. Detailed operating instructions for the extrusion system can be found in Appendix A.6.

The extrusion system is equipped with pressure transducers at the SSE outlet to the TSE, at zone 3 of the TSE by the injection ports, and at the TSE exit die. Each barrel section has its own heater, thermocouple and cooling fan. The operating temperature is set and maintained using individual temperature controllers. There are two separate control panels, one for the SSE and one for the TSE. The SSE control panel has 4 temperature controllers and 1 pressure display (from the transducer at the SSE outlet), while the TSE control panel has 12 temperature controllers and 1 pressure reading (from the transducer at zone 3). The transducer at the die has its own display mounted to the side. In this work, the TSE temperature profile was kept constant, meaning that the temperature for each zone was the same along the entire length of the barrel. The SSE has a cooling jacket at the feed throat to
ensure that pellets do not melt before entering the screw. The SSE was operated with an increasing temperature profile in order to build up the pressure needed to push the melt through in the subsequent zones. The first zone was held below the melting temperature of PET and the last zone was kept at reaction temperature.

The system includes a 200-lb. capacity dryer, used to remove water from the PET before feeding it to the extruder. There is also an 18” vent stuffer at zone 8 whose purpose is to allow volatiles to escape while keeping the polymer inside the main barrel. While the extrusion system can be configured with a vacuum vent as shown in Figure 4.1, the vent was not used in the experiments discussed in this work and the vent port was sealed off.

Although the Leistritz 34mm TSE has a fairly large average throughput capacity, about 100 lbs/hr, the system output is limited by the single-screw extruder whose average capacity is closer to 10-20 lbs/hr. The 2 extruders cannot be decoupled, and therefore understanding of how the operation of either affects the overall performance is crucial.

4.2.1 Screw Configuration

The extrusion system was purchased by Praxair and was configured for devolatilization as shown in Figure 4.1. With the tools for pulling the screws from the TSE unavailable, changes to the screw configuration could not be made. The screw configuration for the TSE is represented as closely as possible in Figure 4.2:
Conveying elements move the polymer by positive displacement. Shearing elements are generally present to aid with melting. The reverse conveying elements form a melt seal by causing the polymer to back up and fill the entire barrel in those areas, while kneading blocks provide mixing just past the injection port zones.

4.2.2 DIE MODIFICATION

The original configuration of the extruder die was intended to feed a strand of polymer, exiting at a 30° angle (downward) to a water bath. The diameter of the die was quite large (approx. 3-4 mm) although no exact value is given in the technical data. Figure 4.3 shows the original die configuration as received from Praxair.
This die configuration was changed during the course of this research. The reason for the change was due to the low melt viscosity of the oligomeric product in the extruder. Because of the low melt viscosity (on the order of 1 Poise), the extruder could not build up back pressure and no melt seal was formed in the lower end of the barrel. This resulted in the inability of the extruder to hold pressure, and volatiles escaped at the die with the extrudate instead of at the vent stuffer.

Once this result was observed, we changed the die configuration in an attempt to build back pressure. We added a valve to the die face with the intent of being able to open and close the valve at will and change the amount of pressure applied to the outgoing polymer. The new configuration is shown in the schematic in Figure 4.4.
The pressure transducer at the die was added during this modification, allowing the pressure at the die to be monitored during reaction. While the addition of the valve did provide some back pressure, it was still not enough to allow the extruder to hold pressure during depolymerization.

4.3 Mass Flow Rates and Residence Time

Initial experiments to characterize the behavior of the extruder system in the absence of any reaction were undertaken before an exhaust system was installed in the laboratory and thus were performed using polystyrene (PS) prior to studies with PET.

Using general-purpose PS (Atofina GPPS 535, MFI = 4.0 g/10 min, high heat crystal PS designed for extrusion, injection molding and blow molding), the mass flow characteristics of
the coupled system were studied at 200°C. Figure 4.5 shows the dependence of mass throughput on both the feed rate of PS (equivalent to single-screw speed, or SSE, in rpm) and the speed of the twin-screw:

![Graph showing extruder throughput for GPPS at 200°C.](image)

**FIGURE 4.5** Extruder Throughput for GPPS at 200°C.

With the exception of very high feed rates, the speed of the twin-screw extruder does not affect the mass flow rate. The flow rate is, however, strongly dependent on the feed rate, or single-screw speed. Results in Figure 4.6, isolated from Figure 4.3 at a single twin-screw speed, indicate that this dependence is quite linear:
Average residence times in the extruder were calculated from tracer experiments done at 200°C with PS and pulse injections of carbon black. The only residence time we are able to measure is that of the coupled system, the time the polymer takes to go through both the SSE and TSE. For the reaction, which occurs only along the length of the TSE, the residence times would be shorter than the times measured here.

Table 4.1 shows an example of times measured for the carbon black pulse with PS at 200°C for a TSE speed of 200 rpm. The average residence time is taken to be the average of the difference between the time the first carbon black was seen in the extrudate and the time the last evidence of carbon black was seen.
In Figure 4.7, it can be seen that, like the throughput, the residence time is not a strong function of twin-screw speed and depends mainly on the feed rate of the SSE into the twin-screw extruder.

<table>
<thead>
<tr>
<th>SSE Speed (rpm)</th>
<th>Mass Flow Rate (g/min)</th>
<th>Time to first exit (s)</th>
<th>Time to final exit (s)</th>
<th>Average time (s)</th>
<th>Average time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>194</td>
<td>162</td>
<td>252</td>
<td>207</td>
<td>3.45</td>
</tr>
<tr>
<td>80</td>
<td>170</td>
<td>165</td>
<td>280</td>
<td>222.5</td>
<td>3.71</td>
</tr>
<tr>
<td>70</td>
<td>160</td>
<td>175</td>
<td>302</td>
<td>238.5</td>
<td>3.98</td>
</tr>
<tr>
<td>60</td>
<td>144</td>
<td>200</td>
<td>310</td>
<td>255</td>
<td>4.25</td>
</tr>
<tr>
<td>50</td>
<td>117</td>
<td>213</td>
<td>372</td>
<td>292.5</td>
<td>4.88</td>
</tr>
<tr>
<td>40</td>
<td>97</td>
<td>245</td>
<td>424</td>
<td>334.5</td>
<td>5.58</td>
</tr>
<tr>
<td>30</td>
<td>80</td>
<td>300</td>
<td>528</td>
<td>414</td>
<td>6.90</td>
</tr>
<tr>
<td>20</td>
<td>54</td>
<td>390</td>
<td>778</td>
<td>584</td>
<td>9.73</td>
</tr>
<tr>
<td>10</td>
<td>31</td>
<td>694</td>
<td>1298</td>
<td>996</td>
<td>16.60</td>
</tr>
</tbody>
</table>

TABLE 4.1 Recorded values of residence time with PS, T = 200°C, TSE speed = 200 rpm.

In Figure 4.7, it can be seen that, like the throughput, the residence time is not a strong function of twin-screw speed and depends mainly on the feed rate of the SSE into the twin-screw extruder.

FIGURE 4.7 Average residence time in TSE System for GPPS at 200°C.

Mass flow experiments were later repeated with Voridian PET (bottle-grade resin CB12, IV = 0.83) at 260°C, shown in Figure 4.8. The dependence of the extruder throughput on the single-screw speed, or feed rate of PET, is evident.
Results shown in Figure 4.9, isolated from Figure 4.8 at a single twin-screw speed, again indicate that this dependence is quite linear.

It is interesting to note the differences in throughput between PS and PET when comparing Figures 4.5 and 4.8. The flow rates for PS are consistently lower than those for PET at the same screw speeds. This is due to the difference in melt-flow index (MFI) between the two.
The MFI for PS is reported as 4.0 g/10 min while the MFI for PET is typically much higher, indicating a lower melt viscosity. Typical melt viscosities for PS are 1-2 orders of magnitude greater than those for PET.\textsuperscript{4-6}

\subsection*{4.4 Residence Time Distribution}

It is worthwhile here to include a brief discussion of residence time distribution (RTD) in the extruder. Although we did not measure this in our research, there is data available in the literature showing how the RTD changes with different operating conditions for the same twin-screw extruder, a Leistritz 34 mm counter-rotating TSE. Shon et al.\textsuperscript{1} studied the RTD in the LSM 34-GG using a commercial polypropylene (PP) (Quantum Chemical, MFI = 5 g/10 min). It should be made clear that Shon et al. were not working with a coupled extruder system, as we are, but rather a single TSE. They measured the RTD by making pulse inputs of aluminum flakes (about 5 grams) into the hopper and collecting extrudate samples every 10-20 seconds after injection until the Al flakes disappeared from the extrudate. The PP was burned away from the samples in a furnace, leaving behind the Al flakes which were collected and weighed.

Shon et al. found that the RTD in the LSM 34-GG is a strong function of the extruder throughput. The higher the throughput, the more narrow the RTD. A narrow RTD suggests that the extruder is operating close to plug-flow conditions without much longitudinal
mixing. As the RTD spreads, the operation moves away from plug-flow. At very broad RTDs, the extruder behaves more like a CSTR with high levels of mixing.

Shon et al. saw a very narrow pulse for a PP throughput of 334 g/min. The pulse did not broaden too much except at the lowest throughput of 84 g/min. The variance, a measure of how broad the pulse is, is shown in Figure 4.10 for different throughputs at a fixed TSE speed of 200 rpm.

At a fixed throughput, Shon et al. saw that increasing the TSE screw speed decreased the mean residence time of polymer in the extruder and also the variance, related to the RTD. They compared these results for different screw configurations, however. Two of the configurations had only conveying elements, but the third had a melt seal, kneading blocks and mixing blocks in addition to conveying elements – most similar to our configuration.

![Figure 4.10](image-url)  
**Figure 4.10** Variance versus throughput for PP at 210°C, TSE = 200 rpm.¹
They found that for this particular configuration, described as “most typical of industrial practices”, the changes in mean residence time and variance were small from one TSE speed to another. These values were compared at their lowest throughput (84 g/min), for which they had the largest variance compared to other throughputs (Figure 4.10). Figure 4.11 shows that while changes in variance with TSE speed are small, increasing the TSE speed decreases the variance.

![Figure 4.11 Variance vs. TSE speed for PP at 210°C at a throughput of 84 g/min.](image)

In our residence time measurements with PS, prior to using carbon black, we attempted to mimic the Al tracer experiments conducted by Shon et al. Without a furnace, however, we found that measuring the Al flake concentration in the extrudate would be rather intensive. Figure 4.12 shows qualitatively what the extrudate looked like over time after a pulse injection of 1 g of Al flakes to PS at 200°C, a SSE speed of 50 rpm and a TSE speed of 250
rpm. Samples were collected in 1 minute increments upon first seeing Al flakes in the extrudate.

**Figure 4.12** PS extrudate samples collected over time after 1 g Al flake pulse, increasing time from L-R and top-bottom in 1 minute increments, 15 min. total.

Figure 4.12 shows that the pulse distribution at these operating conditions was fairly narrow, as high concentrations of Al flakes exited within the first 6 minutes. The tail of the distribution is long, but the concentration of Al flakes appears to drop quickly after minute 6. The samples at minutes 10 and 11 appear darker due to a discoloration of the PS, not the presence of Al flakes. Samples 10 and 11 are translucent (as opposed to those from minutes 2-6) and have a brownish hue due to contamination. The brownish hue is more obvious in the photograph in sample 12.
4.5 REFERENCES


CHAPTER 5

CONTINUOUS GLYCOLYSIS OF PET VIA REACTIVE EXTRUSION

5.1 INTRODUCTION

Yalcinyuva et al.\textsuperscript{1} have done work on the hydrolysis of PET in a twin-screw extruder and studied the influence of a number of process characteristics found in reactive extrusion. The most notable of these are the operating temperature, reaction pressure, screw speed and solvent feed rate. They found that increasing the operating temperature from 265°C-300°C increased the extent of depolymerization. An increase in the reaction pressure from 0-700 psi resulted in faster reaction rates and higher conversions. There existed an optimal value of screw speed – the reaction rate increased from a screw speed of 10 rpm to 20 rpm, but decreased beyond that. This was probably due to an increase in shear mixing but subsequent decrease in residence time. Increasing the steam flow rate was seen to reduce the residence time, attributed to both an increase in reactor pressure and a lowering of viscosity in the reactor (due to depolymerization and a larger stoichiometric excess of water).

The group concluded that the steam feed rate should be low in order to achieve the desired balance between residence time and conversion. For the PET hydrolysis reaction, the stoichiometric ratio of water to PET required for complete hydrolysis is only 0.1875:1 by weight. They report that the optimal water to PET weight ratio is about 0.5:1 in the extruder, compared to a value of 5.1:1 reported by Campanelli for the batch reactor process\textsuperscript{2,3}. Both
groups were able to achieve essentially complete depolymerization, with Yalcinyuva et al. obtaining products with an average DP$_n$ of 1-2 in a residence time of 2.45 minutes. Thus, operating conditions in the extruder provided greater efficiency for the depolymerization reaction when compared to the batch reactor.

5.2 EXPERIMENTAL PROCEDURE

5.2.1 MATERIALS

Bottle-grade (CB12) virgin PET resin used in this study was donated by Voridian ($M_w = 55,000$; PDI = 2.8; IV=0.82-0.84). Ethylene glycol (purity $> 99\%$) from Acros Organics and liquid carbon dioxide (purity $> 99.8\%$) from National Welders were used as received.

5.2.2 EXTRUDER OPERATION

In the experiments discussed here, EG and supercritical CO$_2$ were fed to the system using Isco 260-D continuous flow syringe pumps. The EG and CO$_2$ were fed at room temperature in varying weight ratios to polymer feed rate. The CO$_2$ was fed at supercritical conditions and the pressure in the CO$_2$ feed line was maintained using a micro-metering valve from High Pressure Equipment. Unless specified otherwise, the TSE was operated at 260°C along the entire length of the barrel and its screw speed was kept constant at 150 rpm while the single-
screw speed, or feed rate, was varied. Further details about the extrusion system can be found in Chapter 4. Reaction products were collected at the die onto a metal plate, allowed to cool and taken for preparation for analysis. They were ground to a powder and dried in a vacuum oven for at least 12 hours at 90-100°C, after which analysis was performed.

5.2.3 SAMPLE ANALYSIS

Oligomeric products collected from the extruder were analyzed by intrinsic viscosity (IV) measurement using a Rheotek RPV-1 Polymer Viscometer (please see Appendix A.7 for operating procedure). The measurements were done at 25°C in a 60:40 (vol.) mixture of phenol/tetrachloroethane (Harrell Industries). Values of $M_n$ were calculated from the measured IV using a correlation from the literature. Results are given in terms of IV (dl/g) or DP$_n$ (calculated from $M_n$).

5.2.4 PET CHARACTERIZATION

The Voridian CB12 resin was characterized by intrinsic viscosity measurements in phenol:TCE (60:40 v/v) at 25°C. The IV was found to be 0.83, consistent with the values given by Voridian. Elemental analysis was also performed to determine which residual catalysts might be present in the polymer and in what amount. The metals that were targeted were zinc, lead, copper, manganese and antimony, consistent with typical catalysts used for melt polymerization and solid-state polymerization. The values for zinc, lead, copper and
manganese were all less than 1 ppm, but the concentration of antimony was about 30 ppm. This suggests the presence of an antimony oxide catalyst in the feed polymer, although no additional catalyst was added prior to or during the depolymerization experiments. Additional work was done to look at the melting point and the melt viscosity of the Voridian CB12 resin. Results of this work can be found in Appendix A.8.

5.3 RESULTS AND DISCUSSION

The twin-screw extrusion system is a very effective means of depolymerizing PET via glycolysis. Figure 5.1 shows the behavior of the extruder over time (elapsed operating time where time zero is the time at which the EG feed was started) at fixed reaction conditions for EG:PET = 0.01 and EG:PET = 0.03 (w/w).

![Figure 5.1 Glycolytic extrusion of PET over time, T=260°C, P=1 atm.](image-url)
In Figure 5.1, it can be seen that the extruder reaches steady-state within 10 minutes (about one residence time) and is able to produce a uniform product over time. Increasing the feed ratio of EG:PET (w/w) increases the extent of depolymerization.

**Figure 5.2** Effect of varying feed rate and EG:PET ratio on glycolysis at 260°C, 1 atm.

Figure 5.2 shows results obtained at steady-state. Increasing the feed ratio of EG:PET (w/w) increases the extent of depolymerization. Increasing the PET feed rate, or shortening the residence time, has the effect of decreasing the extent of depolymerization. At the highest EG:PET ratio and longest reaction time, the product obtained has an IV of 0.11, corresponding to a decrease in molecular weight (M_n) from 20,000 to 2,500 and a decrease in the degree of polymerization (DP_n) from 102 to just 13.
Using a value of $1.0 \pm 0.4$ for $K_{dep}$, measured experimentally (results in Chapter 3) and consistent with literature values, we are able to predict the $DP_n$ that would be reached at equilibrium for a given EG:PET feed ratio (a sample calculation can be found in Appendix A.9). The range of $DP_{eq}$ is plotted in Figure 5.2 along with the experimental data. At the longest residence time (feed rate = 55 g/min), the final $DP_n$ of the product comes very close to the equilibrium $DP_n$ for all EG:PET feed ratios. As we decrease the amount of time available for reaction, we move further away from equilibrium, suggesting a need to increase the reaction rate in order to operate at higher feed rates and still achieve low DP products.

Preliminary results on a single-screw extruder suggested that the use of scCO$_2$ as a plasticizer for the polymer during glycolysis could lower the melt viscosity of the PET and increase the diffusivity of EG into the polymer, resulting in higher reaction rates in the extruder.$^5$ The results demonstrated that an increase in CO$_2$ feed rate at supercritical conditions was able to nearly double the reaction rate in the single-screw system. In our experiments with scCO$_2$ in the TSE system, shown in Table 5.1, we see no influence of scCO$_2$ on the extent of depolymerization.

<table>
<thead>
<tr>
<th>EG:PET Feed Ratio</th>
<th>Pressure CO$_2$ (psi)</th>
<th>Weight % CO$_2$</th>
<th>Product $DP_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>0</td>
<td>0</td>
<td>52</td>
</tr>
<tr>
<td>0.005</td>
<td>1200</td>
<td>4.5</td>
<td>52</td>
</tr>
<tr>
<td>0.005</td>
<td>1500</td>
<td>8</td>
<td>55</td>
</tr>
<tr>
<td>0.04</td>
<td>0</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>0.04</td>
<td>1500</td>
<td>2</td>
<td>18</td>
</tr>
</tbody>
</table>

**Table 5.1** Addition of scCO$_2$ at 260°C, 100 g/min PET.
Upon closer inspection of glycolysis results for an EG:PET ratio of 0.01 (Figure 5.3), no dependence of the extent of depolymerization on the PET feed rate is observed. We conclude from this that the reaction is reaching equilibrium at even the shortest residence times (highest feed rates) for this feed ratio. This explains why CO₂ showed no influence on the reaction at the EG:PET=0.005 feed ratio; most likely the system was already at equilibrium without the presence of CO₂. Figure 5.3 shows that the DP of the products is coming very close to the predicted range of values for DP_{eq}. There is no observed dependence of the extent of depolymerization on the PET feed rate for this EG:PET ratio. Even at this low EG:PET feed rate, greater than 65% depolymerization is achieved.

**Figure 5.3** Varying PET feed rate at 260°C, EG:PET = 0.01 (w/w), 1 atm.
The influence of twin-screw speed on the extent of depolymerization was also investigated. The intrinsic viscosity of products at 5 different operating conditions and 4 different TSE speeds are plotted in Figure 5.4. For all conditions, there does not appear to be any influence of the TSE speed on the final IV of the products.

The influence of temperature on this reaction was investigated and is shown in Table 5.2. Operating at a fixed polymer feed rate of 100 g/min and an EG:PET ratio of 0.04, as the reaction temperature increases from 230°C-280°C, the extent of depolymerization increases. Although the change in the extent of reaction is modest from one temperature to the next, the operating temperature in the extruder is still a consideration, and increasing the temperature moves the product DPₙ closer to the equilibrium value that is predicted.
While operation at temperatures below the melting point of PET (245°C) is possible due to the depolymerization that is taking place in the reactor, decreasing the temperature also decreases the extent of depolymerization. There are two parameters changing with temperature in this system. The rate of reaction is certainly seen to increase with an increase in temperature in most, if not all, of the reaction systems discussed in Chapter 2. This would cause an increase in the extent of depolymerization with increasing temperature. In addition, because this reaction is endothermic, it is expected that an increase in temperature would increase the value of $K_{dep}$ and consequently increase the equilibrium extent of depolymerization. Using the $\Delta H_R$ that was estimated for glycolysis in Chapter 3, about +10.9 kJ/mol, and the following equation from Levenspiel\textsuperscript{6}:

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_R}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$  \hspace{1cm} (5.1)$$

where $R$ is the ideal gas constant and $\Delta H_R$ is constant, values of $K_{dep}$ at different temperatures can be calculated (using the $K_{dep}$ measured at 260°C as a basis), along with the predicted

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Flow Rate PET (g/min)</th>
<th>Product DP$_n$</th>
<th>$K_{dep}$</th>
<th>Predicted DP$_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>100</td>
<td>20</td>
<td>0.95 ± 0.4</td>
<td>10-12</td>
</tr>
<tr>
<td>260</td>
<td>100</td>
<td>16</td>
<td>1.1 ± 0.4</td>
<td>10-12</td>
</tr>
<tr>
<td>280</td>
<td>100</td>
<td>13</td>
<td>1.2 ± 0.4</td>
<td>10-11</td>
</tr>
</tbody>
</table>
range of DP values at equilibrium. These are shown in Table 5.2 alongside the experimental DP values of the products.

It is interesting to look at how sensitive the value of $D_{peq}$ that is predicted is to the value used for $K_{dep}$. Figure 5.5 shows this relationship for an EG:PET feed ratio of 0.4. For values of $K_{dep}$ that are close to 0.5 and above, the value of the predicted equilibrium DP does not change much. It is only below 0.5 that the value of $K_{dep}$ strongly affects the equilibrium value of $DP_n$.

No additional increase in the extent of depolymerization was seen upon increasing the EG:PET feed ratio to values greater than 0.04. In fact, Figure 5.6 shows that the final $DP_n$ of the products even appears to increase slightly.
Because the reaction is carried out at atmospheric pressure and at a temperature above the boiling point of EG, there is a limit to the amount of EG that is soluble in the molten polymer. Any additional EG added above that limit simply vaporizes. In order to manipulate this behavior, the extruder would need to be pressurized. However, due to the low melt viscosity of the oligomers, the extruder is unable to hold pressure by traditional means. This also helps explain the result of our experiment with scCO₂ at the EG:PET = 0.04 feed ratio (Table 5.1). Without holding CO₂ in the extruder at supercritical conditions, it cannot assist the reaction.

**Figure 5.6** Results of glycolysis at EG:PET ratios of 0.04 and above, 260°C, 1 atm.
Further work has been done to look at the ability to depolymerize a post-consumer bottle-grade PET resin as well as the ability to repolymerize the oligomers collected from the extruder. The results can be found in Appendix A.10 and A.11, respectively.

5.4 CONCLUSIONS

We present a novel process for the depolymerization of PET via glycolysis. Results clearly show that using an extruder as a reactor is a highly effective means of depolymerizing the polymer. In a residence time of just 10 minutes, we are able to reduce the IV more than 85%, from 0.83 to 0.11, corresponding to a decrease in $D_{P_n}$ from 102 to 13. Without pressurizing the extruder, we see that increasing the residence time (by decreasing the feed rate of PET) or increasing the EG:PET ratio leads to an increase in conversion. We observe no influence of the TSE speed on the reaction, while increasing the temperature causes a modest increase in the extent of depolymerization. With modification of the extruder to hold pressure, the use of supercritical CO$_2$ in the system should allow for the production of equally low-molecular-weight oligomers at higher throughputs and lower operating temperatures.

This research could play a role in reducing the considerable amount of bottle-grade PET resin that is manufactured from virgin materials, resulting in a significant environmental and economic impact. Furthermore, this approach should be applicable to any step-growth polymer, including nyons and polycarbonates.
5.5 REFERENCES


CHAPTER 6
CONCLUSIONS AND FUTURE DIRECTIONS

6.1 CONCLUSIONS

This work explored the area of continuous depolymerization of PET via glycolysis. We introduced a novel reaction system for glycolysis, using a twin-screw extruder to carry out the depolymerization. This goal of this work was to obtain a low-molecular-weight oligomer of BHET that could be used for repolymerization to obtain a high-molecular-weight PET synthesized from 100% post-consumer materials.

We began by studying the equilibrium of the melt glycolysis of PET, in order to understand the system and be able to target a specific DP end product. Using batch reactors at 260°C, we found that the value of the equilibrium constant for the depolymerization, \( K_{\text{dep}} \), was close to 1.0 for various starting ratios of EG:PET. When we increased the reaction temperature to 270°C, we found that the equilibrium constant changed slightly but was still close to a value of 1. Using this information, we were able to predict equilibrium DP values for a given EG:PET feed ratio.

We also conducted experiments to characterize the behavior of the twin-screw extrusion system as a reactor. We found that the polymer throughput depends almost entirely on the
single-screw speed and is independent of the twin-screw speed for all but the lowest twin-screw speeds. For a constant twin-screw speed, the dependence of the polymer throughput on the single-screw speed is linear.

From there, we began glycolysis experiments in the twin-screw extruder system at 260°C and atmospheric pressure. Our results clearly show that using an extruder as a reactor for the glycolysis of PET is a highly effective means of depolymerizing the polymer. In a residence time of just 10 minutes, we are able to reduce the IV more than 85%, from 0.83 to 0.11, with a final DP\textsubscript{n} of 13.

Without pressurizing the extruder, we see that increasing the residence time (by decreasing the feed rate of PET) or increasing the EG:PET ratio leads to an increase in conversion. At EG:PET ratios of 0.01 or lower, we are able to reach equilibrium in the system even at our lowest feed rates, producing oligomers with a DP\textsubscript{n} of about 30. As we increase the EG:PET ratio beyond 0.04, we do not see any additional depolymerization due to vaporization of the EG in the extruder. We do not see any influence of changing the TSE speed on the extent of depolymerization reached for a given operating condition. By increasing the reaction temperature, modest increases in the rate extent of depolymerization are seen.
6.2 Future Directions

This research has laid the groundwork for many other potential research areas. Primarily, this method of depolymerization can be used for recycling other step-growth polymers. For example, there is a good deal of research in the area of depolymerization of polycarbonates, mainly using batch reactors with reaction times on the order of hours. Fundamentally, there is no reason why depolymerization of polycarbonate could not be done in an extruder on a continuous basis, increasing throughputs and decreasing reaction times. The same is true for the recycling of nylons or polyurethanes.

Another continuation of this work would certainly be to improve the design of the extruder for this type of reaction. As is, it is not configured to handle such low-viscosity melts and therefore screw features that are designed to maintain back pressure are ineffective when faced with such a low-molecular-weight oligomer. Modifying the design to incorporate the ability to maintain pressure in the extruder would open up a whole new area of study for the depolymerization system.

While holding EG at a pressure above its vapor pressure would allow for production of oligomers with even lower degrees of polymerization than those already obtained, the ability to hold pressure and take advantage of the devolatilization capability of the twin-screw extruder begs the question: could the benefits of supercritical CO₂ as a plasticizer in the system be exploited to increase reaction rates and diffusivity of EG into the polymer?
While increasing the operating temperature of the barrel is seen to lower the final DP$_n$ of the product, the use of supercritical CO$_2$ in the system should increase reaction rates, allowing for the production of equally low-molecular-weight oligomers at higher throughputs and lower operating temperatures. Another promising feature of using scCO$_2$ is that it can be used for supercritical fluid extraction. In other words, it has the potential to extract volatile organic contaminants that may be found in a post-consumer PET stream, e.g. acetaldehyde. This would allow for simultaneous reaction and extraction and lead to more purified low-molecular-weight oligomers. Ideally, the EG and CO$_2$ would be recycled to the system, further increasing the cost-efficiency of the process.
APPENDIX
A.1 OPERATING PROCEDURE FOR BATCH GLYCOLYSIS EXPERIMENTS

A.1.1 BATCH GLYCOLYSIS REACTIONS

1. Turn on the Fisher Hi-Temperature Bath and allow it to reach the desired temperature at which you want the reaction to take place. It is helpful to use a thermocouple submerged in the bath to record the temperature.

2. While the bath is heating up, prepare the reactors (in our case, HiP 5 mL Micro-reactors) by charging them with the desired amounts (by weight) of EG and PET. Add stainless steel mixing balls (about 5) to the reactor. Seal the reactors to the required torque (about 70 ft-lbs) and use a bit of lubricant on the threads to keep the seal tight.

3. Once the bath temperature is reached, place the reactors into the bath using tongs. The bath temperature should stabilize in 5-10 minutes.

4. Once the reactors have been placed in the bath, start the oscillation by turning on the compressed air, which will be directed to either end of the pneumatic cylinder via a solenoid valve (power must be ON for solenoid valve).

5. Once the desired reaction time is reached, remove reactors from the bath with tongs and immediately submerge in room temperature water to quench the reaction.

6. Once cooled, open the reactors and remove the reaction product using a thin spatula or other similar item.
7. Collect the products to dry in a vacuum oven at about 90-100°C for at least 8 hours before analysis.

**Figure A.1.1** Schematic of Reactors in Oil Bath with oscillation.

**Figure A.1.2** Picture of Temperature Bath Set-up.
A.1.2 HYDROXYL END-GROUP TITRATION

Materials:

Pyridine
Acetic anhydride
Distilled Water
Dry Dichloroethane
0.1 N KOH
Phenolphthalein indicator
Procedure:

1. Accurately weigh ~ 0.5g of sample
2. Add to 10 mL of 88:12 (v/v) pyridine and acetic anhydride in a round-bottom flask
3. Fit with a vertical reflux condenser and reflux in a boiling water bath with stirring for about 2 hours (or until dissolved)
4. Cool mixture to room temperature
5. Hydrolyze by adding 100 mL of chilled water
6. Add 20 mL of dichloroethane with vigorous stirring
7. Titrate with 0.1 N KOH standard using a phenolphthalein indicator

In the acetylation reaction that is carried out here, the OH end groups of the product are converted to carboxylic acid end groups. Because residual EG is removed by drying, the remaining OH groups are representative of the end groups on the oligomer chain. To determine the total number of end groups present, the solution is titrated with KOH until neutral. The result is the hydroxyl number, or OH#, which represents the number of equivalents of KOH required to neutralize the solution.
A.2 Sample Calculation of $K_{dep}$

Once the hydroxyl value is obtained from the titration using Equation (3.1), it has units of mg KOH per gram of sample. An equation was derived to use that value to calculate the $DP_n$ of the sample. We first find the number of moles of KOH, equivalent to the # of moles of OH end groups. Then, to find the number of chains that are present in the product, we divide the value by 2 since each chain has 2 OH end groups (from the HEE group). The equation we use is the following:

$$DP_n = \frac{2 \cdot 56000 \left( \frac{mgKOH}{molKOH} \right)}{MW_{RU} \left( \frac{gRU}{molRU} \right) \cdot OH \left( \frac{mgKOH}{gRU} \right)}$$

where RU is the repeat unit of PET, and MW_{RU} is 192 g/mol. Once this calculation is done, it gives the following units: mol RU/ (mol OH groups/2). Remembering that the mol OH groups (= mol KOH) divided by 2 gives us the total number of chains, we then have: # RU/# chains, which is the definition of DP. The value of DP that we calculate is an average value for the system. Once DP is known, we can use the following mole table to find the values of HEE, EDE, and EG needed to solve for $K_{dep}$ using Equation (3.4).

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Starting Value (mol/mol RU)</th>
<th>Equilibrium Value (mol/mol RU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDE</td>
<td>$DP_0$</td>
<td>$(DP_0/DP)-1$</td>
</tr>
<tr>
<td>HEE</td>
<td>2</td>
<td>$2 \cdot (DP_0/DP)$</td>
</tr>
<tr>
<td>EG</td>
<td>$MW_{RU}/MW_{EG}$</td>
<td>$EG_0 - ((DP_0/DP)-1)$</td>
</tr>
</tbody>
</table>
The value of $D P_0$ is 102 for the Voridian PET, calculated from the known molecular weight of the starting material, $M_n = 20,000$, whereas the value $D P$ refers to the final $D P$ reaction in the system after reaction.

Example:

For a measured value of the OH# of 340:

$$D P_n = \frac{2 \cdot 56000 (mg KOH / mol KOH)}{192 (g RU / mol RU) \cdot 340 (mg KOH / g RU)} = 1.72$$
A.3 DERIVATION OF EQUATION 3.7

The glycolysis reaction can be written as follows, assuming the reaction only takes place in the liquid phase and that there is no monomer or polymer in the vapor phase:

\[
\frac{d}{dt} (V_L P_i) = V_L \left\{ -k_f P_i (i-1) C_E + k_b \sum_{j=1}^{i-1} P_j P_{i-j} + 2k_f \sum_{j=i+1}^{\infty} P_j C_E - 2k_b \sum_{j=i+1}^{\infty} P_i P_{j-i} \right\}
\]  \hspace{1cm} (3.6)

where \( C_E \) is the molar concentration of EG in the liquid phase, \( P_i \) is the molar concentration of polymer with DP = \( i \), \( V_L \) is the volume of the reactor, \( k_f \) is the rate constant for depolymerization in the forward direction and \( k_b \) is the rate constant for the backward reaction (i.e. \( K_{dep} \) is defined as \( k_f/k_b \)).

Rewritten, Equation 3.6 becomes:

\[
\frac{1}{V_L} \frac{d}{dt} (V_L P_i) = -k_f C_E \left[ P_i (i-1) - 2 \sum_{j=i+1}^{\infty} P_j \right] + k_b \left[ \sum_{j=1}^{i-1} P_j P_{i-j} - 2P_i \sum_{j=i+1}^{\infty} P_{j-i} \right]
\]  \hspace{1cm} (3.6.1)

Now, let

\[
G = \sum_{i=1}^{\infty} s^i P_i
\]

Substituting this expression for the generating function, \( G \), into Equation 3.6.1 yields:

\[
\frac{1}{V_L} \frac{d}{dt} (V_L s^i P_i) = -k_f C_E \left[ P_i (i-1) s^i - 2 \sum_{j=i+1}^{\infty} s^j P_j \right] + k_b \left[ s^i \sum_{j=1}^{i-1} P_j P_{i-j} - 2P_i s^i \sum_{j=i+1}^{\infty} P_{j-i} \right]
\]  \hspace{1cm} (3.6.2)
Taking the summation over this expression from i=1 to infinity yields the following expression:

\[
\sum_{i=1}^\infty \frac{1}{V_L} \frac{d}{dt} (V_L s^i P_i) = -k_f C_E \left[ \sum_{i=1}^\infty (i-1)s^i P_i - 2 \sum_{i=1}^\infty (s + s^2 + \ldots + s^{i-1})P_i \right] + k_b \left[ \sum_{i=1}^\infty P_i s^i \right] - 2t \sum_{j=1}^\infty P_j \sum_{j=1}^\infty P_j \tag{3.6.3}
\]

Writing this expression back in terms of G results in:

\[
\frac{1}{V_L} \frac{d}{dt} (V_L G) = -k_f C_E \left[ s \frac{dG}{ds} - G - 2 \sum_{i=1}^\infty (s + s^2 + \ldots + s^{i-1})P_i \right] + k_b \left[ G^2 - 2G \sum_{j=1}^\infty P_j \right] \tag{3.6.4}
\]

Since

\[
\mu_0 = \lim_{s \to 1} (G) = \sum P_j \tag{3.6.5}
\]

the following expression can be found:

\[
\frac{1}{V_L} \frac{d}{dt} (V_L G) = -k_f C_E \left[ s \frac{dG}{ds} - G - 2 \sum_{i=1}^\infty \frac{s(s^{i-1} - 1)}{(i-1)}P_i \right] + k_b \left[ G^2 - 2G \mu_0 \right] \tag{3.6.6}
\]

From this point, since the definitions of \( \mu_1 \) is

\[
\mu_1 = \lim_{s \to 1} \left( s \frac{dG}{ds} \right) \tag{3.6.7}
\]

we find that for s=1,

\[
\frac{1}{V_L} \frac{d}{dt} (V_L \mu_0) = k_f C_E (\mu_1 - \mu_0) - k_b \mu_0^2 \tag{3.7}
\]
A.4 DERIVATION OF EQUATION 3.10

The depolymerization of PET can be written as follows:

\[
[A - A]_{n+m} + C_E \leftrightarrow [A - A]_n + [A - A]_m
\]  
(3.9)

Writing an expression for equilibrium using equation (3.9) yields the following expression:

\[
K_{dep} = \frac{[A - A]_n [A - A]_m}{[A - A]_{n+m} C_E}
\]  
(3.9.1)

Assuming that \(K_{dep}\) does not depend on \(n\) or \(m\) and that the BHET monomer \([A-A]_1\) is one of the products, the expression becomes:

\[
K_{dep} = \frac{[A - A]_1 [A - A]_{n+m-1}}{[A - A]_{n+m} C_E}
\]  
(3.9.2)

Letting \(n+m = n\),

\[
K_{dep} = \frac{[A - A]_1 [A - A]_{n-1}}{[A - A]_n C_E}
\]  
(3.9.3)

or

\[
\frac{1}{K_{dep}} \frac{[A - A]_1}{C_E} [A - A]_{n-1} = \frac{[A - A]_n}{[A - A]_{n+1}} = \alpha
\]  
(3.9.4)
Then, we find that:

\[
\frac{[A - A]_2}{[A - A]_1} = \frac{[A - A]_3}{[A - A]_2} = \alpha \tag{3.9.5}
\]

and that

\[
\frac{[A - A]_3}{[A - A]_1} = \alpha^2 \tag{3.9.6}
\]

Rewritten, this becomes:

\[
\frac{[A - A]_n}{[A - A]_k} = \alpha^{n-1} \tag{3.10}
\]

where

\[
\alpha = \frac{1}{K_{dep}} \frac{[A - A]_1}{C_E} \tag{3.11}
\]
A.5 Estimating the Solubility of EG in BHET Using Aspen

In order to estimate the solubility of EG in PET, we assumed that the solubility of EG in PET was the same as its solubility in BHET monomer. This assumption was made because we had data available for BHET monomer that was not available for PET which enabled the use of ASPEN (UNIFAC) to predict the phase behavior of the EG-BHET system.

A T-x-y plot was made and is shown below, assuming that P is constant at 1 atm.

**Figure A.5.1** T-x-y diagram for EG-BHET system at 1 atm.
From this diagram, the mole fraction of EG in BHET at 260°C was estimated to be 0.32. Again, we assumed that the mole fraction of EG in PET at 260°C was also 0.32 for the calculations that led to the plot shown in Figure 3.4.
A.6 OPERATING PROCEDURE FOR TWIN-SCREW EXTRUSION SYSTEM

CAUTION: The extruder barrel gets extremely hot (up to 300°C). While operating the extruder, it is mandatory to wear heat resistant gloves, close-toed shoes and safety glasses. Do not wear loose clothing that may get caught on the screw or barrels.

A.6.1 EXTRUDER OPERATION:

1. Turn on the power for the single-screw extruder, located at the back of the operating panel, and the power to the twin-screw extruder, located below the operating panel on the machine itself.

2. Turn on the chiller/water supply to the feed throat of the single-screw extruder. The feed throat temperature should be kept close to room temperature.

3. Turn ventilation blower on.

4. Turn power on for vent-stuffer device (if using).

5. If required, set the temperature of the different extruder zones from the control panel.
   
   NOTE: Twin-screw extruder temperatures are in °C while single-screw extruder
temperatures are in °F. The extruder set temperature will depend on the melting temperature of the polymer being used.

6. For hygroscopic material (like PET), refer to the procedure for the drier.

7. Once the temperature reaches the set points (about 1 hour), the extruder is ready for operation. Check the temperature of the last zone (die zone) of the twin-screw extruder and the valve (if in place) as it takes more time for these areas to reach the set point.

8. Fill the hopper on top of the single screw extruder with the material to be processed.

9. Adjust the vent-stuffer speed to desired rpm if using.

10. Turn on the twin-screw motor using the green button on the panel. You will hear the motor fan turn on. Adjust the twin-screw speed to desired rpm. NOTE: It is important to turn on the twin-screw extruder before the single-screw extruder. If not, the plastic being pushed by the single-screw extruder will have nowhere to go and will build up pressure until the rupture disc at the adapter blows.

11. Turn on the single-screw motor by pushing the green button on the panel. Turn the single screw speed knob to desired rpm. A squeaking sound is normal as solid pellets
are ground into the screw. Keep an eye on the motor amps for both the single and twin-screw extruder to make sure the motor does not overload.

12. The single-screw speed can be increased incrementally, depending on the polymer. If the amp reading goes above 25 on the twin-screw extruder, decrease the speed of the single-screw extruder.

13. If nothing happens after 5-10 minutes (TSE amps don’t increase, etc.), then the single-screw feed throat may be plugged and will require cleaning. Refer to the feed throat cleaning procedure.

14. Turn on the water for the water trough if planning to collect a filament strand to feed to the pelletizer.

15. Once a steady-state has been reached in the extruder, you may collect samples (i.e. for mass flow calibration, etc.) or begin reaction.
A.6.2 Procedure for Injecting EG into the Extruder

1. An ISCO 260-D continuous flow syringe pump is used to feed EG into the extruder.
   Make sure the power to the pump is on and that the pumps are full. If operating in
   continuous mode, make sure inlet tubing is placed in solvent bottle.

2. Set the desired operation mode (typically continuous constant flow).

3. Set the desired flow rate in mL/min. This will depend on the desired EG:PET ratio.

4. Start the pump at the set flow rate. NOTE: The EG feeding into the extruder will
   have to overcome a certain pressure of the polymer in order to push the polymer out
   of the injection port and allow the EG to enter the extruder barrel. You should see
   the pump pressure increase for a while after which the pressure will drop to a
   negative value, at which point the EG will have entered the extruder barrel. This can
   take a long time at low flow rates; it may be helpful to use a higher flow rate for 1-5
   minutes in order to build up pressure in the tubing before dropping back to your
   desired flow rate.

5. Once the EG has been injected, you should see the TSE amps drop dramatically as the
   depolymerization reaction proceeds. Your product will be a very low viscosity
   oligomer. NOTE: The oligomeric product must build up pressure in the twin-screw
   extruder to push out the non-reacted PET before it can exit. BE CAREFUL! Once
   the non-reacted PET is pushed out, the low viscosity product will exit at a high
   pressure and can spray everywhere. It is highly recommended to use a safety screen
   at the exit and to not stand too close to the extruder die when this is about to happen.
**Shut-down:**

When you are finished running the reaction, simply stop the EG pump and allow all of the reacted product to exit the extruder. Once the TSE amps are back up and pure PET is exiting, you may continue with normal shut-down procedure.

**A.6.3 Procedure for Injecting Supercritical CO₂ Into the Extruder**

**Startup:**

1. CO₂ cylinders with dip tubes are used and CO₂ is pressurized and fed using an Isco 260-D continuous flow syringe pump.
2. Check the amps on the twin-screw extruder. Without reaction, the amps should be between 15-18 to form the proper melt seals in the extruder.
3. Open the cylinder to refill the syringe pump. Leave open if operating in continuous mode.
4. Set desired CO₂ flow rate and start the pump.
5. Open or close the back pressure regulator on the injection line to achieve the desired pressure of CO₂. (You should see a pressure reading at the transducer by the injection port, on the display panel on the TSE operating panel.)
6. Adjust CO₂ pressure and flow rate as needed. If running a reaction simultaneously, start CO₂ flow BEFORE starting reaction.
7. When finished using CO₂, simply stop the pump, close the CO₂ cylinder and turn off power to the pump. Continue with normal shut-down procedure.

A.6.4 SHUT-DOWN PROCEDURE

1. Let the material run out of the hopper before stopping the single-screw extruder. Let the twin-screw run at 50-150 rpm until the amps drop low and only a very thin strand is exiting at the die.
2. Stop the screws, first by turning the rpm down to zero and then by hitting the red power button on the panel. Turn off power to both extruders (and vent stuffer if using).
3. Turn off heaters for valve section.
4. Leave cooling water on for up to 1 hour as feed throat will still be hot, then turn off.
5. Turn off ventilation blower.

A.6.5 PROCEDURE FOR USING PLASTICS DRYER

1. Some hygroscopic material (like PET and nylon) need to be dried before processing in the extruder. For drying conditions, refer to a plastic handbook (for PET, typically 350°F for 8-10 hours).
2. Since the hopper is installed on a stand which is 9-10 feet above the ground, moveable stairs are required to load the hopper. The hopper capacity is 200 lbs.

3. Load the hopper with polymer to be dried so that it is at least ¾ full. This is required for proper operation of the dryer. Plastic can be loaded from the top of the hopper or from the side door.

4. For routing drying, the dryer can be programmed to turn on by itself and drying can be performed unattended. Refer to dryer manual for programming details.

5. Once the plastic is dry, the plastic can be fed directly to hopper on single-screw extruder.

A.6.6 Procedure to Clean the Feed Throat

1. Stop both the extruders.

2. Empty the hopper out of plastic and remove the hopper (lift off).

3. Take out the bolts connecting the feed throat to the extruder body.

4. Disconnect water tubing connected to the feed throat.

5. In most cases, the feed throat can be removed easily and cleaned.

6. If there is melted plastic between the screw and feed throat, use a puller/crowbar/monkey wrench to remove the feed throat.

7. Clean the screw and feed throat, put back the feed throat, connected the water supply and bolt the feed throat to the extruder.
A.7 OPERATING PROCEDURE FOR RHEOTEK RPV-1 POLYMER VISCOMETER

A.7.1 GENERAL INFORMATION:

- It is important when choosing the solvent/temperature of operation for your sample that you have a good MW correlation from the literature (Mark-Houwink parameters) if you are interested in using the IV to get an estimate of the MW.

- You will need dilute solutions, about 4-5 concentrations for each sample. As a general rule, for samples with MW on the order of 10,000, the concentration should be on the order of $10^{-3}$ g/mL, for MW on the order of 100,000, the concentration should be on the order of $10^{-4}$ g/mL. For each run on the viscometer, you need between 7-12 mL of your solution.

- Each solution MUST be filtered before running it in the viscometer. The IV is VERY sensitive to dust particles.

- It takes about 20 minutes to run one solution on the viscometer (including cleaning). It usually takes about an hour for the temperature of the bath to stabilize once it is turned on.
A.7.2 Running the Viscometer:

1. Turn on computer that controls the RPV-1 and open the RPV-1 program.

2. Turn on the power to the temperature bath, chiller and viscometer.

3. Once the temperature bath is on, make sure the bath temperature is set to the desired value within the RPV-1 program.

4. Wait for the bath temperature to stabilize.

5. While temperature is stabilizing, it is a good idea to clean the viscometer you are using with the solvent you are using and let it dry before running any solvent/solution. ** You must turn on the vacuum pump to do this and leave it on while running your samples!

6. Once the bath temperature is stable, run the pure solvent in the viscometer to get the solvent flow time. Make sure the vacuum pump is ON before running solvent and samples.

7. Once the solvent flow time is measured, begin to run your solutions and make sure that the flow time of the solvent you ran is selected. For each sample, keep the same name and change only the concentrations for each solution you made for that sample (should be 4-5 solutions per sample).
8. While you are running, make sure that the solvent jars for the viscometer are filled with acetone and your solvent, and make sure that the waste bottle does not overfill.

9. When you are finished, make sure to let the final cleaning and drying steps go to completion. Turn off the vacuum pump, the temperature bath, chiller and viscometer, and shut down the computer.

10. Make sure to empty all of the waste in the waste bottle into a separate waste container for disposal.

A.7.3 SOLUTION PREPARATION:

1. Using 20 mL vials, weigh 4-5 amounts between 0.01 and 0.05 g into individual vials.

2. Add 10 mL of solvent and a small stir bar to each.

3. Allow sample to dissolve in solvent under stirring and heat if necessary, but be careful not to allow the solvent to evaporate. Keep caps on vials tightly closed.

4. Once the sample has completely dissolved, allow the sample to cool and make sure it is thoroughly mixed.
5. Using a syringe, remove solution from vial, add syringe filter to syringe and filter the solution into a clean vial (make sure to use vials that come with caps on so that there is no dust accumulation inside them). The solution is now ready to be run in the viscometer. Always run prepared solutions within 1 day of preparation to ensure consistent results.

A.7.4 Viscometer Tips:

- If the viscometer is having trouble drawing your sample, adjust the strength of the pump. A slower draw time is better than a fast one (draw time between 30-60 s).

- If the viscometer is having trouble getting reproducible values for a particular solution, it will time it up to 5 times and after that, the viscometer is set to automatically clean. If you see that the solution is having trouble, turn off auto-clean or you will lose your sample without getting a result. (Typically, only 2 runs are needed).

- When choosing a viscometer, your pure solvent flow time should be at least 60 s. If it is lower, the viscometer should not be used with that solvent.

- The RPV-1 at NC State is configured with 2 viscometers. The viscometer on the left (Viscometer #1) is meant for aqueous systems. For this work, only Viscometer #2 was used.
The melting point of the virgin resin from Voridian (CB12) was measured via differential scanning calorimetry (DSC) using a TA Q-100 with a heating rate of 10°C/min. The result of the scan is shown below in Figure A.8.1:

![DSC thermogram for Voridian CB12 PET resin.](image)

**FIGURE A.8.1** DSC thermogram for Voridian CB12 PET resin.

The melt rheology of the virgin resin and oligomeric products were also tested using a TA Instruments Stress Rheometer (AR-2000). The complex viscosity was measured at 260°C using oscillatory shear. Figure A.8.2 shows that the difference in melt viscosity of the virgin resin and the low-molecular-weight oligomers changes by several orders of magnitude as the depolymerization proceeds to larger extents, reaching melt viscosities on the order of 1 Pa·s.
**Figure A.8.2** Dynamic rheology of Voridian CB12 and glycolysis products at 260°C.
A.9 Sample Calculation of Predicted Equilibrium DP

Using the same stoichiometric table from Appendix A.2, one can see that we have values for the functional group concentrations at equilibrium written in terms of DP.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Starting Value (mol/mol RU)</th>
<th>Equilibrium Value (mol/mol RU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDE</td>
<td>DP₀</td>
<td>(DP₀/DP)-1</td>
</tr>
<tr>
<td>HEE</td>
<td>2</td>
<td>2 · (DP₀/DP)</td>
</tr>
<tr>
<td>EG</td>
<td>MW₉U/MW₉G</td>
<td>EG₀ – ((DP₀/DP)-1)</td>
</tr>
</tbody>
</table>

Plugging the expressions in the table for concentrations of the functional groups at equilibrium into Equation 3.4 yields an expression for $K_{dep}$ in terms of DPₙ.

$$K_{dep} = \frac{\left(2 \cdot \frac{DP₀}{DP}\right)^2}{\left(\frac{DP₀}{DP} - 1\right) \cdot \left(EG₀ - \left(\frac{DP₀}{DP} - 1\right)\right)}$$

If the value of $K_{dep}$ is known, we can set the left-hand-side of the equation equal to 1, and use solver in Excel to find a value of DPₙ that sets the right-hand-side of the equation equal to 1 as well. The table below shows that for an EG:PET feed ratio of 1 (w/w) and assuming a value for $K_{dep}$ of 1, the predicted equilibrium DP is 1.68.

<table>
<thead>
<tr>
<th>EG:PET (w/w)</th>
<th>HEEₑq</th>
<th>EDEₑq</th>
<th>EGₑq</th>
<th>$K_{dep}$</th>
<th>RHS</th>
<th>DPₑq</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>122</td>
<td>41</td>
<td>256</td>
<td>1</td>
<td>0.9999999617</td>
<td>1.68</td>
</tr>
</tbody>
</table>
A.10 Depolymerization of Post-Consumer PET in TSE via Glycolysis

Using the same procedure that is detailed in Chapters 4 & 5, a post-consumer PET resin (RPET) was also depolymerized via glycolysis in the TSE at 260°C. The resin (100% post-consumer PET, Grade: NLP Clear) was donated by Phoenix Technologies in Bowling Green, OH. The following properties were provided for the resin:

- IV = 0.71 dL/g
- Melting Point = 246°C
- Crystallinity = 36%

The IV of the resin was measured using the same method and viscometer described in Chapter 5. At 25°C in 3:2 PhOH/TCE, the IV was found to be 0.73 dL/g.

The RPET was glycolyzed at the following conditions: T = 260°C, RPET feed rate = 55 g/min, with the following results shown in Table A.10.1.

<table>
<thead>
<tr>
<th>EG:PET (w/w)</th>
<th>IV (dL/g)</th>
<th>Mₙ (g/mol)</th>
<th>DPₙ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.20</td>
<td>5400</td>
<td>28</td>
</tr>
<tr>
<td>0.04</td>
<td>0.11</td>
<td>2400</td>
<td>13</td>
</tr>
</tbody>
</table>

Table A.10.1 Glycolysis results for RPET resin at 260°C, RPET feed = 55 g/min.
These results (IV & DP values) are the same as those obtained from glycolysis of the Voridian CB12 resin, demonstrating that we are able to reach the same extents of depolymerization with a post-consumer resin as we are with a virgin PET resin.
A.11 Repolymerization of Glycolyzed Oligomers

In order to show that the oligomers we produce via glycolysis can in fact be repolymerized, polymerization experiments were carried out using three different starting materials: one, a BHET oligomer obtained by glycolysis of virgin PET with an average DP ≅ 15, IV = 0.11 dL/g (RPOLY1), two, an oligomer obtained by glycolysis of the RPET resin with an average DP ≅ 15, IV = 0.11 dL/g (RPOLY2), and three, an oligomer obtained by glycolysis of the RPET resin with an average DP ≅ 30, IV = 0.20 dL/g (RPOLY3).

Experimental Procedure:

The procedure for melt polymerization was loosely adapted from Lin et al.\textsuperscript{1} and is as follows:

1. Place 50 g of oligomer and 200 ppm antimony oxide in a 500 mL round flask.
2. Purge the flask with nitrogen for 30 minutes.
3. Heat the flask to 275°C.
4. Allow reaction to proceed for 1 hour with nitrogen flow and agitation.
5. After 1 hour, stop the nitrogen flow and pull a vacuum using a vacuum pump.
6. Allow reaction to proceed for 2 hours.
7. After 2 hours, stop the reaction and collect the product.

The results from the repolymerization experiments are shown in the Table A.11.1. Using the procedure described, we are able to repolymerize the oligomeric products to a higher IV. While slightly different results are obtained for post-consumer resin products versus virgin resin products, both do undergo repolymerization. It may be possible to further increase the final IV obtained by optimizing the reaction conditions/procedure.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Starting IV (dL/g)</th>
<th>Final IV (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPOLY1</td>
<td>0.114</td>
<td>0.443</td>
</tr>
<tr>
<td>RPOLY2</td>
<td>0.110</td>
<td>0.347</td>
</tr>
<tr>
<td>RPOLY3</td>
<td>0.197</td>
<td>0.298</td>
</tr>
</tbody>
</table>