**ABSTRACT**

PANG, KYEONG. Novel Manufacturing, Spinning, and Characterization of Polyesters based on 1,2-Ethanediol and 1,3-Propanediol. (Under the direction of Richard Kotek and Alan Tonelli)

Poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT), poly(ethylene isophthalate) (PEI), and poly(trimethylene isophthalate) (PTI) were synthesized in a Parr reactor and melt-spun. Thermal and physical properties of the as-synthesized polymers and melt-spun fibers were determined. As-synthesized PEI and PTI were amorphous polymers and did not show any melting peaks by DSC analysis. All the polymers were thermally stable (TGA analysis). Amorphous films were made by a melt-press method with PET and PEI for determination of CO₂ gas barrier properties. PEI, which has the meta-linkage of ester groups on the phenyl ring, had much lower CO₂ gas permeability around one tenth that of PET, which has the para-linkage of ester groups on the phenyl ring. This is because in PET the phenyl rings are substituted in the para (1,4) positions, which allows for their facile flipping, effectively permitting gases to pass through. However, the meta-substituted phenyl rings in PEI do not permit such ring flipping, and thus PEI may be more suitable for barrier applications. The coalesced PEI was prepared from the inclusion compound of PEI with γ-cyclodextrin. The coalesced PEI may have retained partially highly extended and parallel chains from the narrow channels of the inclusion compound, resulting in better/tighter
packing among the PEI chains and exhibited a higher glass-transition temperature. Cyclic oligoesters of PET, PTT, PEI, and PTI were prepared by cyclo-depolymerization of these polyesters. The cyclic oligoesters were mixtures of different sized cyclic oligomers. PET cyclic oligomers showed four melting peaks at 59, 122, 194, and 276 °C. The cyclic oligomers of PTT, PEI, and PTI showed single melting peaks at 241, 335 °C and 147 °C, respectively. The cyclic oligoesters could be converted to linear polyesters by ring-opening polymerization. PTT was also prepared by ring-opening polymerization of its cyclic dimer obtained as a by-product in the conventional manufacturing plant. Antimony, tin, and titanium catalysts were used with various concentrations. The highest molecular weight, 40,000 g/mol was obtained when 0.25 mol% of titanium(IV) butoxide was used.
NOVEL MANUFACTURING, SPINNING, AND CHARACTERIZATION OF
POLYESTERS BASED ON 1,2-ETHANEDIOL AND 1,3-PROPANEDIOL

by
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Doctor of Philosophy

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APPROVED BY:

_________________________________  ____________________________
Co-chair of Advisory Committee  Co-chair of Advisory Committee
Dedicated to my mother, my father,
my husband, Jeesang Hwang, and my son, Ethan.
BIOGRAPHY

KYEONG PANG was born on November 20, 1973 in Seoul, Korea. She attended Youngpa girl's high school and graduated in 1992. In February 1996, she graduated from the Soongsil University with a Bachelor of Science Degree in Textile Engineering. She then accepted a full time job in Londonfog Korean branch office for managing garment factory. In 1998 she quit her job to continue her studies, so she returned to Soongsil University and obtained her Masters of Science in Textile Chemistry in February 2000. After graduation she worked as an intern researcher supported by Korea Science and Engineering Foundation in the same university for one and a half year. In July 2001, she came to United States with her husband and enrolled in North Carolina State University where she worked towards her Doctor of Philosophy in Fiber and Polymer Science.

She was getting married to Jeesang Hwang, a classmate in May 2001, and has a one-year-old son, Ethan.
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SUMMARY

Linear aliphatic polyesters were first synthesized by Carothers and coworkers. However; they could not be commercialized because of low melting points and poor hydrolytic stability. Later Whinfield and Dickson synthesized poly(ethylene terephthalate) (PET), which had a high melting temperature (265° C) and good hydrolytic stability. Subsequently many other aromatic polyesters have been studied. Among these polyesters, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) have been produced commercially for more than 50 years. Poly(trimethylene terephthalate) (PTT) was commercialized very recently. Usually polymers prepared by condensation polymerization contain cyclic molecules along with the linear chains. The cyclic oligomers create problems during fiber processing, such as spinning and dyeing. Recently the cyclic oligomers and their ring-opening polymerization have become of interest. The cyclic oligomers can be prepared as the major products by using high-dilution methods, polymer-supported techniques, and cyclo-depolymerization. The cyclic oligoesters can then be used as feedstocks for their ring-opening polymerization. Ring-opening polymerization has some advantages over the conventional polymerization method. The conventional method requires high temperature and high vacuum, and a small molecule by-product is produced. The overall reaction is long, varying from 5 to 10 hrs. On the other hand, ring-opening polymerizations do not produce any by-product and the reaction occurs at atmospheric pressure. Furthermore, the process is very rapid. Polyesters like PET and PBT have been increasingly used due to their good physical properties. One of these important properties is action as a gas barrier, so polyester film is
widely used as a packaging material. The characteristics of polyesters depend on structure, symmetry, and conformational features. Polyesters with collinear attachment of ethylene glycol diester to the phenyl rings, like PET and PTT, may experience in flipping of the phenyl rings. However, the phenyl rings of the polyesters with non-collinear attachment to the phenyl ring, like PEN and poly(ethylene isophthalate) (PEI), cannot be flipped. The flipping of these rings may allow gases to permeate through, as the gas molecules may use them much like a trap door or valve. Thus polyesters with non-collinear linkages can have better gas barrier properties than the others.

1. INTRODUCTION

Linear polyesters were first synthesized by Carothers and coworkers. The fiber drawn from the molten polyester of trimethylene glycol and hexadecamethylene dicarboxylic acid was the first synthetic fiber. However, it had a low melting point and poor hydrolytic stability. Later Whinfield and Dickson discovered poly(ethylene terephthalate) (PET), which was high melting (265°C) and had good hydrolytic stability. Subsequently many other aromatic polyesters have been studied. Among these polyesters, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) have been produced commercially for more than 50 years. Poly(trimethylene terephthalate) (PTT) was commercialized very recently. PET is used world wide for the production of synthetic fibers, films, beverage bottles, and molded plastic parts, because of its good physical properties.
PET is manufactured from ethylene glycol (EG) and terephthalic acid (TPA) or dimethyl terephthalate (DMT). The polymerization has two steps: esterification reaction and condensation reaction. Usually during the polymerization reaction there are some side reactions including thermal degradation, hydrolysis, cyclization, and diethylene glycol (DEG) formation. These side reactions influence physical properties of the polymer.

Recently cyclic oligomers (that are produced by the side reactions) and their ring-opening polymerization have become of interest. The ring-opening polymerization has some advantages over conventional polymerization methods. The ring-opening polymerization does not produce any by-product, such as water or methanol, and the reaction occurs at much lower temperatures and atmospheric pressure. Furthermore, the process is very quick.

In this chapter, details of the conventional synthetic methods and the ring-opening synthetic method are mentioned. In addition, some important physical properties of polyesters are also described.

2. CONVENTIONAL SYNTHETIC METHODS

Polyesters, especially poly(ethylene terephthalate) was manufactured as an industrial products by ICI (UK, 1949) and Du Pont (USA, 1953) soon after the technology of manufacturing was developed by Whinfield and Dickson in 1946. Polyester is typically manufactured by two routes: transesterification of dimethylester with diol to form an intermediate diester and oligomers, followed by polycondensation to form the polymer; or direct esterification of the diacid with the diol, followed by polycondensation. In this section, these conventional methods for the PET manufacture will be mentioned.
2. 1. Raw Materials

Raw materials for PET manufacture are terephthalic acid (TPA) or dimethyl terephthalate (DMT) and ethylene glycol (EG). Recently, pure TPA has replaced DMT as the preferred raw material after development of purified terephthalic acid (TPA) by Amoco [1]. Crude TPA is produced by the air oxidation of p-xylene in acetic acid. 4-carboxy-benzaldehyde (4-CBA) is one of the main impurities present in the crude. An aldehyde group in 4-CBA acts as a chain terminator in the PET polymerization. Because this contaminant has a very similar structure to that of TPA, it is difficult to remove 4-CBA from TPA. In the Amoco process [2, 5], TPA can be purified by dissolution in water and hydrogenation with a granular 0.5% Pd/C catalyst. It can also be purified by recrystallization from a solution of the mixture solvent phenol and water [3], and crystal aging in 90% acetic acid [4]. Table 1 shows the raw materials for different aromatic polyesters.

2. 2. Polymerization Method

The polyesters are prepared in two steps: the first step, prepolymerization forming bis-(2-hydroxyethyl) terephthalate (BHET), the precursor for the second step, melt polycondensation. Figure 1 shows the schemes for the reactions.

First step: Prepolymerization
a. Transesterification [1, 15, 16, 17]

The monomers for the transesterification reaction are DMT and EG. A reactor is charged with DMT and EG with 1:2.1~2.3 molar ratio and catalysts. A slow stream of nitrogen is passed through the apparatus. The reaction temperature should be 170~210°C. During the reaction methanol is collected into a graduated receiver as a byproduct to allow estimation of the extent of conversion. When the methanol distills over, the reaction is completed and bis-(2-hydroxyethyl) terephthalate (BHET) is obtained in the first step.

b. Direct esterification [17, 18, 19, 21, 22, 23]

This reaction is a heterogeneous reaction with monomers of TA and EG. The mixture of monomers should be charged as a slurry type, because TA is hard to dissolve in EG. The molar ratio TA to EG is 1:1.5 ~ 3, and the reaction temperature is usually 240 ~ 260°C. According to Kang’s paper, the use of a large monomer feed ratio and high reaction temperature are useful to enhance the solubility of TA [23]. Generally, catalysts are not used for this reaction, since the acid functional groups of TA can catalyze the reaction. Water formed from the reaction as a byproduct should be collected for the estimation of the reaction conversion. In the commercial reaction, some PET prepolymer (BHET) is added in order to shorten the reaction time.
Second step: Polycondensation [20, 21]

BHET produced from the transesterification reaction or direct esterification reaction is gradually heated to 280°C. The reactor is evacuated to low pressure (below 1 mm Hg), while maintaining the temperature at 280°C. In this step, EG is collected as a by-product. The overall reaction time that includes the esterification and the polycondensation processes is long and usually varies from 5 to 10 hrs.

2. 3. Polymerization Kinetics Under Various Reaction Conditions

Tomita [24] reported stirring speed and reaction temperature effects on the polycondensation kinetics. Higher intrinsic viscosity (IV) was obtained at faster stirring speed, and the reaction time was shortened at higher reaction temperature. Chegolya et al. [21] used terephthalic acid (TA) as an additive during the polycondensation process of the prepolymer produced by the direct esterification method. The polycondensation process proceeded two to three times faster with the introduction of certain amounts of TPA into the prepolymer. They suggested that the carboxylic acid of TPA formed an ion pair from autoprotolysis and the proton ion catalyzed the reaction [21].

2. 4. Catalysts and Additives

In many commercial processes, manganese or zinc salts are used as the catalysts for the transesterification step. Antimony oxide based catalyst is typically added as the
polycondensation catalyst in either the transesterification or direct esterification processes outlined above. A phosphorous-based stabilizer is commonly added with the catalysts to prevent color-forming degradation reactions during the polycondensation process and subsequent polymer processing.

Many researchers have studied the effects of various catalysts for both reactions: transesterification and polycondensation. Tomita et al. [16] investigated the rate of transesterification of DMT with EG and the effect of catalysts. They used zinc acetate and manganese acetate with various concentrations as the catalysts. While it requires about 2 hours reaction time to obtain high conversion with the zinc acetate catalytic system, high conversion is obtained in 20 minutes with the manganese catalytic system, using optimum concentrations for each. The optimum concentrations of zinc acetate and manganese acetate are $1 \times 10^{-3}$ and $5 \times 10^{-3}$ mol / mol DMT, respectively. The electrophilic mechanism for metallic catalysts is known as the following [16, 25].

\[ \text{RC}_1^\text{OR} + \text{RC}_2^\text{OR} \xrightarrow{\text{Cat}^+} \text{RC}_1^\text{OR} \xrightarrow{\text{HOCH}_2\text{CH}_2\text{OH}} \text{RC}_2^\text{OR} \xrightarrow{\text{Cat}^-} \text{R}_1\text{C}_2^\text{OR} \xrightarrow{\text{HOCH}_2\text{CH}_2\text{OH}} \text{R}_1\text{C}_2^\text{OR} \xrightarrow{\text{Cat}^+} \text{RC}_1^\text{OR} \]

Shah et al. investigated the effect of various metallic catalysts on the polycondensation reaction of BHET [25]. They polymerized PET with different concentrations of catalysts and
reaction temperatures and compared their intrinsic viscosities. The results show that titanium based catalyst is the most active catalyst and antimony and tin based catalysts are less active. The activity of the polycondensation catalysts increases in the order Ti > Sn > Sb > Mn > Pb [25]. However, a titanium-based catalyst has a disadvantage; it imparts a yellow color to the polymer. The optimum concentration for titanium based catalyst (K TiOx), tin based catalyst (SnO(But)_2), and antimony based catalyst (Sb_2O_3) are 1.5 X 10^{-4}, 2 X 10^{-4}, and 2.4 X 10^{-4} mol/mol BHET, respectively [25]. In the presence of excess catalyst, intrinsic viscosity falls because there is a competition for catalyst between the sites responsible for the polymerization reaction like chain end groups and the sites on formed polymer like ester oxygen [25]. The intrinsic viscosity increased with an increase in the reaction temperature in the range of 270 ~ 295°C [25].

MacDonald studied several catalysts for polycondensation in his paper [29]. Antimony oxide historically emerged as the catalyst of choice, because it demonstrates a good balance between catalytic activity in the presence of the phosphorous-based stabilizer, color, and cost [29]. Germanium oxide is also used. Although it is a more active catalyst than antimony oxide, its high cost precludes common uses for commercial PET [29]. Titanium-based catalysts are also very active relative to antimony, but they are prone to hydrolysis to form oxoalkoxides which have reduced activity and make the polymer hazy. Two different mechanisms were proposed by Ravindranath (Figure 2a,) and Parshall and Ittel (Figure 2b). Although the catalytic mechanism is still poorly understood, the “Ravindranath mechanism” involves a hexacoordinate metal catalyst molecule. In the primary step, the metal ion coordinates to the ester carbonyl bond. The coordination of the ester carbonyl bond lowers the electron density of the carbonyl carbon atom and facilitates nucleophilic attack. Then the
reaction proceeds via the activation of the hydroxyl end-group of a different incoming polymer chain, which attacks the positively polarized carbonyl carbon, and then a new ester bond and metal glycolate species are generated through intramolecular rearrangement (Figure 2). The other mechanism proposed by Parshall and Ittel involves a pentacoordinate metal center. In this mechanism the hydroxyl end-groups of two different incoming polymer chain ends coordinate to the metal center in the form of alkoxide ligands. Intramolecular rearrangement within the coordination sphere then results in the formation of a new ester linkage, which couples the two growing polymer chains, thereby generating new metal glycolate species (Figure 2).

Generally, in industrial production thermal stabilizers are added to prevent thermal degradation during the polycondensation step. Trimethylphosphate (TMP), triethylphosphate (TEP), triphenylphosphate (TPP) and phosphoric acid (H₃PO₄) are widely used as thermal stabilizers. Gumther et al. reported small amounts of triphenyl phosphate (a widely used thermal stabilizer) did not influence the molecular weight, but an amount larger than 0.04 mol % caused a decrease in molecular weight [26].

Karayannidis et al. [28] studied the effect of catalysts in the synthesis of poly(trimethylene terephthalate) (PTT). They synthesized PTT from TPA and 1,3-propanediol (PDO) in the presence of various catalytic systems using the direct technique that is used for PET. Table 2 shows their results. They obtained high molecular weight PTT polymer when titanium tetrabutoxide (TBOT) was used as catalyst for both esterification and polycondensation steps. Although PET becomes yellow when titanium compounds are used for its production, in Shah’s study [25], titanium tetrabutoxide did not show such effects for the PTT polymer [28].
2. 5. Solid-state Polymerization

Like PET, condensation polymers undergo further polycondensation in the solid state at temperatures between their glass transition temperature and their crystalline melting temperature. This phenomenon has been widely used to produce very high molecular weight (> 30,000 number average molecular weight) PET for injection or blow molding applications, because a number average molecular weight of only 15,000 ~ 25,000 g/mol can be acquired by the common melt polymerization process. The solid-state polymerization of PET is carried out at around 220 ~ 230° C for 10 ~ 30 hours [7, 8, 9, 10]. The polymer chip from the polycondensation reaction is first crystallized to prevent sintering and then heated at a temperature roughly 20° C below the melt temperature either in a vacuum or in a hot inert gas in a device that agitates the solid. Schiavone synthesized low molecular weight (IV of around 0.18 dl/g) PET copolyesters with low levels (3 ~ 9 mole %) of isophthalic acid and polymerized them in the solid state at 210 ~ 240° C for 24 hours [6]. From the solid-state polymerization, he obtained higher IVs of 0.4 ~ 0.65 dl/g, for the copolyesters. In addition, the copolyesters had higher melting point and a higher crystallinity than conventional PET.

2. 6. Copolymerization

Copolymerization is one of the most attractive techniques to differentiate the properties of PET and to overcome some of its undesirable properties, such as pilling, low moisture regain,
static charge build up, poor dyeability and adhesion to metals due to high glass transition temperature, and poor processability due to high melting temperature. A large variety of copolyesters can be obtained from the combination of different monomers. For example, 1,3-propanediol, 1,4-butanediol and isophthalic acid can be added to improve dyeability of PET because poly(trimethylene terephthalate) (PTT), poly(butylene isophthalate) (PBI) and poly(ethylene isophthalate) (PEI) have a lower glass transition temperature and crystallinity, so they absorb dye more easily [11, 12, 13]. In addition, films of PET copolymers with 1,4-butanediol or isophthalic acid have improved adhesion to metal plates and gave excellent shock resistance and barrier properties against corrosive compounds [14]. Also, it has been reported that PET copolymer with poly(ethylene naphthalate) or poly(ethylene isophthalate) can be used to increase the gas barrier properties of PET [30, 37, 78, 81, 82]. Copolymers of PET have gained significant commercial interest since the addition of some other polyesters, such as PEN and PEI, into PET, which tend to improve gas barrier properties. Loss of CO₂ from carbonated beverage packages and O₂ ingress from the atmosphere into packages containing oxygen-sensitive products can limit shelf life, so improved gas barrier properties can increase package performance. Recently, poly(ethylene terephthalate-co-ethylene isophthalate) (PETI) copolymer has been investigated by several researchers [11, 30, 31-36]. The thermal behavior and tensile properties of the copolymers were investigated [11, 30]. Their glass transition temperatures decreased with the composition of PEI [11, 30]. The melting temperature also decreased with the composition of PEI, but when the composition was above 20 %, the copolymers were amorphous (no melting temperature exists in DSC analysis). Karayannidis et al. [11] reported that PET and its copolymers with 10 and 20 % of PEI composition could be classified as a hard and tough material having relatively high
Young’s modulus, high tensile strength, high elongation at break, and necking phenomenon, however the copolymers with higher composition of PEI and PEI homopolymer could be classified as a soft and tough material [11]. Ree et al. [30-32] and Gu et al. [34] investigated crystallization behavior and kinetics of the PETI copolymers. The copolymers showed less crystallizability, lower crystallization rate and even become totally amorphous when the composition of PEI was above 20 %. Also, the equilibrium crystallization temperature and melting temperature decrease with the composition of PEI, indicating the crystals of copolymers grow imperfectly [30-32]. The above copolymerization by melt polycondensation of each of the monomers leads to random copolymers when the composition ratio is close to 1. Munoz-Guerra et al. [36] prepared block copolymers by using physical and melt blending procedure. Some of the blends showed higher Young’s modulus or maximum tensile stress than PET homopolymer. However all blends showed very low elongation at break.

3. NOVEL SYNTHETIC METHODS

3.1. Cyclic Oligoesters

Usually polymers prepared by condensation polymerization contain cyclic molecules along with the linear chains. Conventionally produced polyesters also contain small amounts of cyclic low molecular weight oligomers. The cyclic oligomers create problems during PET fiber processing, such as spinning and dyeing, and they should be removed. They can be usually extracted from the polymer product by the Soxhlet extraction method with some
solvents like chloroform [53, 58, 60, 61], dioxane [58, 59], dichloromethane [62], or xylene [40, 62]. They can also be removed with dissolution methods [42, 58]. The polyester is dissolved in a solvent, such as phenol and tetrachloroethane mixture, dimethyl formamide and 1,1,1,3,3,3-hexafluoro-2-propanol. The solution is cooled down and then a non-solvent is added (dioxane or chloroform), which precipitates the polymer. The solution is filtered and evaporated to get dry oligomers.

3.1.1. Extraction of cyclic oligomers from polyesters

Ross et al. [38] isolated one percent of a solid from extraction of PET film in a Soxhlet apparatus. The solid had a melting temperature at 325~327°C. They found that the solid had the cyclic trimer structure (Figure 3, [GT]₃) from the result of carbon-hydrogen analysis. Goodman et al. [39] isolated several kinds of low molecular weight components from PET chip and fiber by solvent extraction with boiling 1,4-dioxane or mixed xylenes. Table 3 shows the outline of their extraction procedures. The total amount of the all extracted compounds was 1.3-1.7 percent by weight: 1.4% of compound A, 0.11% of compound B, 0.03% of compound C and 0.07% of compound D. They determined chemical structures of the compounds A, B, C, and D. The chemical structures are shown in Figure 4. A, B, C, and D were identified as cyclic trimer, tetramer, pentamer, and a compound containing two terephthalate units, an ethylene glycol unit, and a DEG unit, respectively (Figure 4). The compounds A, B, and C were heated with catalysts such as antimony oxide or methyl titanate at 275-310°C and they were converted to PET. This reaction was reported as reversible: cyclic oligomer ↔ linear polymer. In the case of D, it converted to a high melting, crystalline,
fiber-forming polymer by heating with antimony oxide as a catalyst for 1 hour at 275°C, but the polymer was not PET. They also reported three possible mechanisms for the cyclic compound formation: (1) cyclization of short chain linear oligomers; (2) attack of a polymer hydroxyl end-group on an ester group in its own chain (back-biting); (3) reaction of interchange among ester groups within or between polymer chains:

\[
\begin{align*}
\text{CO} & \quad \text{O} \\
\text{O} & \quad \text{CO}
\end{align*}
\quad \rightarrow
\begin{align*}
\text{CO} & \\
\text{O}
\end{align*}
+ \quad \begin{align*}
\text{O} & \\
\text{CO}
\end{align*}
\]

or

\[
\begin{align*}
\text{CO} & \quad \text{O} \quad \text{O} \quad \text{CO} \\
\text{O} & \quad \text{CO} \quad \text{CO} \quad \text{O}
\end{align*}
\quad \rightarrow
\begin{align*}
\text{CO} & \\
\text{O}
\end{align*}
+ \quad \begin{align*}
\text{O} & \quad \text{O} \\
\text{OC} & \quad \text{CO}
\end{align*}
+ \quad \begin{align*}
\text{O} &
\end{align*}
\]

They suggested that the cyclic oligomer formation by ester interchange according to reaction (3) was the most plausible mechanism. Peebles et al. [40] isolated and identified linear and cyclic oligomers of PET. In their study, linear oligomers were prepared by melt condensation of BHET with terephthaloyl chloride and cyclic oligomers were synthesized by reacting linear oligomers with the acid chloride at high dilution. They also extracted similar oligomers from PET yarn and chip. Table 4 shows the identity, physical properties, and composition distribution of the cyclic oligomer extracts they determined. The distribution of oligomers is significantly different from that reported by Goodman et al. for their four compounds, and may be because they used different extraction procedures. However, both studies, Goodman et al. [39] and Peebles et al. [40], concluded that the extracts of chip or fiber do not contain
linear oligomers in detectable amounts, and the cyclic oligomers are unavoidably produced during the polymerization.

Berr et al. [41] reported that a high crystalline sublimate was evolved during the last stages of polymerization of PEI and collected on the walls of the reaction tube just above the heated zone. It was found that the sublimate was the cyclic dimer of ethylene isophthalate (Figure 3, [GI]₂) by using hydrolysis in aqueous sulfuric acid and carbon-hydrogen analysis. The melting temperature was the same as that of the cyclic trimer of ethylene terephthalate. The amount of cyclic PEI dimer was 10-15% based on the weight of polymer, which is a much larger amount than that of the cyclic trimer formed in the polymerization of PET. In the case of PEI, it is easier to form cyclic structures of ethylene isophthalate, because of the kinked geometry of the isophthalic acid. The cyclic oligomers of ethylene isophthalate were more volatile than those isolated from PET. Lim et al. [42] extracted small amount of oligomers from the PET-PEI copolymer and separated and analyzed them with HPLC and NMR to identify them. They made polymer solutions with 1,1,1,3,3,3-hexafluoro-2-propanol as a solvent and washed it with large amounts of chloroform to get the precipitate. The obtained precipitate, a mixture of oligomers, was 1.22 wt % of the copolymer. They reported that most of the oligomers consist of cyclic dimer and cyclic trimers, [GI]₂, [GT]₃, [GI]₃, [GT]₂[GI], and [GT][GI]₂, and also the cyclic oligomers have serious effects on the polymer properties. The cyclic oligomers are shown in Figure 3.

These cyclic oligomers have been reported to affect the physical properties of the polyesters and cause some problems in dying or spinning processes, so that they should be removed. Nagahata et al. [43] showed that cyclic-oligomer-free-PET might be obtained from solid-state polymerization. They obtained cyclic dimer of ethylene terephthalate from a drawing
apparatus at a PET film production site and polymerized it in the solid state. They obtained a colorless polymer with a weight-average molecular weight of 36,100 g/mol [43]. The solid-state polymerization was carried out with several catalysts (1,3-dichloro-1,1,3,3-tetrabutyldistannoxane showed the highest catalytic activity), by heating for 3 hours at 200°C under nitrogen in a thermal analysis instrument [43].

3.1.2. Synthesis of cyclic oligoesters

The cyclic oligoesters can be prepared as the major products by using very high dilution conditions. Usually only small amount of cyclic oligomers are formed during the bulk condensation polymerization. However much more cyclic oligomers can be produced under dilute conditions because the local concentrations of reactive chain ends belonging to the same oligomer is much higher under dilute conditions. The syntheses can be conducted by using high-dilution methods, polymer-supported techniques, and cyclo-depolymerizations (ring-chain reaction). The synthetic cyclic oligoesters have been reported to have similar physical properties as those for the cyclic oligomers extracted from polymers. The cyclic oligomers can be used as feedstock for ring-opening polymerization.

a) Direct synthesis

Cyclic oligomers have been prepared by a classical high dilution technique. It is a simple reaction at a high dilution of: a) diol and diacid, b) diacid and diester, c) or diester only. Hamb et al. [56] prepared the cyclic tris(ethylene terephthalate) by refluxing dilute solution
of linear dimer, bis\{β-[4-(β-hydroxyethoxycarbonyl)benzoyloxy]ethyl\} terephthalate in distilled 1-methylnaphthalene with titanium tetraisoproxide as a catalyst for 64 hours. A novel pseudo-high dilution condensation reaction has been developed for preparing cyclic oligomeric alkylene phthalate [45, 46]. The pseudo-high dilution condensation reaction allows high product concentrations and larger quantities, since large volumes of solvent are not necessary [45]. The reaction is carried out by using diol (HO-A-OH) or one bis-(hydroxyalkyl) ester with one diacid chloride (Cl-CO-B-CO-Cl) in the presence of highly sterically unhindered amines such as 1,4-diazabicyclo[2,2,2]octane (DABCO) or a mixture thereof with tertiary amine such as triethylamine or pyridine [45, 46, 65]. They found that if the triethylamine or pyridine was used as the catalyst, only 5 ~11 % ester was formed at room temperature after 1 hour, and the reaction required 24 hours to be completed [45]. However if the sterically unhindered amines like DABCO were used as the catalyst, the reaction can be finished in 15 minutes at room temperature [45]. The amines neutralize the HCl liberated in the reaction and work as nucleophilic catalysts. As a nucleophilic catalyst, the amine attacks the acid chloride to form an intermediate acylammonium salt, which is then attacked by the nucleophilic alcohol. Figure 5 [45] shows the example reaction mechanisms for butylene terephthalate cyclic trimer produced from classical dilution and pseudo-high dilution condensation methods. Nagahata et al. [47, 48] reported that they could synthesize ethylene isophthalate cyclic dimer selectively. Ethylene glycol diacetate and isophthalic acid dimethyl ester and sodium ethoxide were used as starting materials and catalyst, respectively [47]. They obtained cyclic dimers with purity of 98.4 % and the absence of molecules larger than the dimer with this reaction by stirring the starting materials in cyclohexane at 65° C, for 2 hours [47]. They reported that the most important factor is the solvent and the leaving
groups of substrates, and the key point of their method is the progressive reaction in the form of an azeotropic mixture [47]. They also got a polymer from the dimer by using microwave-radiation.

b) Polymer-supported method

The cyclic oligomers can be prepared by using polymer-supported reagents. It was reported that cyclic polyester was prepared by the utilization of an intramolecular alkylation reaction of a ω-bromocarboxylic acid using an anion-exchange resin [49]. Figure 6 (reprinted from reference 49) shows the schematic representation of the polymer-supported synthesis of cyclic polyester. The acid attached to the basic resin by heating leads to condensation of the carboxylate with the halide [49].

c) Cyclo-depolymerization (ring-chain reaction)

These cyclic oligomers can also be obtained by the cyclo-depolymerization (CDP) of linear polyesters. This technique is useful for recycling of polyesters. A typical depolymerization is carried out by refluxing in dilute solution for many hours in the presence of metal catalysts such as organotin or titanate compound [50-55, 57]. Different solvents and catalysts were used for the depolymerization at low concentrations. At the end of the reaction time, the solution is cooled down to a temperature until the polymer is precipitated. Table 5 shows the solvents and catalyst used by these authors. Hamilton et al. [50] prepared cyclic oligomers of tetraethylene glycol terephthalate, tetraethylene glycol isophthalate, tetraethylene glycol
orthophthalate, decamethylene terephthalate, decamethylene isophthalate, and decamethylene orthophthalate from the cyclo-depolymerization of high mass linear polymers prepared by a condensation polymerization reaction. The depolymerization was carried out by solution transesterification of linear polymers during refluxing in dilute solution (100/1 w/w or 30/1 w/w) of chlorobenzene with dibutyltin oxide as a catalyst [50]. Hodge et al. synthesized a series of cyclic oligo(alkylidene isophthalate) [51]. Figure 7 shows the reaction mechanism [51]. For the cyclo-depolymerization, chlorobenzene and 1,2-dichlorobenzene was used as solvents and the catalyst was dibutyltin oxide [51]. They obtained over 98 % of the oligomeric product within 12 hours. They reported that the depolymerization of PEI shows atypical outcome because the cyclic dimer tended to precipitate out during the reaction [51]. It was also reported that the composition of cyclic oligomer mixtures produced by CDP of polymers could be different at different reaction times [51]. The cyclic monomers are produced mainly from polymers with repeat units with more than 16 chain atoms such as polynanomethylene isophthalate or polydecamethylene isophthalate, on the other side, with up to 15 chain atoms per repeating unit the main products are the cyclic dimers [51]. Hodge et al. reported the cyclo-depolymerization of poly(propylene terephthalate) using 1,2-dichlorobenzene and n-butylin oxide as a solvent and a catalyst [52]. The major cyclic oligomer produced was cyclic dimer [52]. Semlyen et al. [53, 54] prepared cyclic oligo(ethylene terephthalate) [53] and cyclic oligo(butylene terephthalate) [54] from commercial PET and PBT chip by refluxing the solution of 1-methyl naphthalene or 1,2-dichlorobenzene with several esterification catalysts [53]. Their products were fractionated with GPC and the typical GPC trace is shown in Figure 8 [53]. They reported that zinc acetate was a very effective catalyst for CDP of PET, and also by increasing the solvent
dilution ratio, the larger cyclic oligomers were formed in good yield [53]. Macknight et al. [57] prepared cyclic oligomers by cyclo-depolymerization from PET waste using titanate catalyst. Their research showed the possibility of PET recycling via the commercial scale preparation of ethylene terephthalate cyclic oligomers. Burch et al. [66] synthesized ethylene terephthalate cyclic oligomers (ETCs) and ethylene isophthalate cyclic oligomers (EICs) by refluxing their linear oligomers or polymer in saturated, unsaturated hydrocarbon, or their mixtures as solvents. They also explored catalysts such as titanium alkoxides, antimony glycoxide, aluminum butoxide, and zirconium ethoxide for cyclic oligomer formation [66].

3.2. Ring-opening Polymerization of Cyclic oligoesters

Many studies on conversion of cyclic oligomers to high molecular weight linear polymer via ring opening polymerizations have been presented. Ring-opening polymerization offers potential advantages relative to the conventional polymerization process [63]. Higher polymer molecular weights can be more easily achieved. Molecular weights as high as 100,000-300,000 g/mol are reported for the ring-opening polymerization, while the highest molecular weights achieved by step polymerization are 40,000-60,000 g/mol. Additionally, there is no by-product in the ring opening polymerizations. The low melt viscosity of the cyclic oligomers allows processing by various techniques, such as pultrusion, resin-transfer molding, melt filtration, or reaction injection molding either concurrent with or just prior to polymerization (Figure 9) [44, 64]. Low viscosities are thought to be very useful for polyesters with high melting points and high melt viscosities such as poly(ethylene naphthalate) or poly(butylene naphthalate) [65]. Cyclics Corporation produces the cyclic
oligomers of butylene terephthalate (CBT), as a mixture of dimer, trimer, and tetramer. These oligomers are made by breaking down poly(butylene terephthalate) (PBT) [64]. CBT can be polymerized back into PBT in the presence of a transesterification catalyst. CBT, in the molten state, can flow like a thermoset resin into the glass or carbon fiber reinforcing material in composites, while the finished product retains the properties of the thermoplastic [64].

High molecular weight polyesters have been prepared by ring-opening polymerization using simple procedures in the presence of various transesterification catalysts [43, 45, 57, 65-68]. The most effective catalysts are usually organotin and organotitanate compounds [46]. In a typical experiment, cyclic oligomers were dried at 80–100°C under vacuum. The reactor was charged with cyclic oligomer and catalyst and heated at the reaction temperature and stirring until all the material was molten in the presence of nitrogen gas. The stirrer usually stopped within seconds as the polymerization was completed. Table 7 shows detailed conditions of ring-opening polymerization by various investigators.

Sugiyama et al. [43] prepared a high molecular weight PET (36,100 g/mol) by the ring opening polymerization of ethylene terephthalate cyclic dimer in the solid state. The polymerization was carried out with various transesterification catalysts: N,N-diethylaniline, 4-dimethyl-aminopyridine, stearic acid lithium salt, p-toluene sulfonic acid, cyclohexyltriphenylphosphonium tetraphenylborate, dibutyltin(IV) dichloride, and 1,3-dichloro-1,1,3,3-tetrabutyl distannoxane. Table 8 shows the efficiencies of the catalysts under various reaction conditions. 1,3-dichloro-1,1,3,3-tetrabutyldistannoxane showed the highest catalytic activity. By using 4 mol % of this catalyst, they obtained 100% conversion and the highest molecular weight PET at 200°C after only 3 minutes. However, this polymerization
was done with very small amounts of monomer (1.3 - 1.6 mg) in the aluminum pans in a thermal analysis instrument [43].

Brunelle et al. prepared high molecular weight PBT and its copolymer with PET via ring-opening polymerization using several catalysts within 10-20 minutes [45]. Among the catalysts, cyclic stannoxane (Figure 10) can initiate the polymerization of cyclic oligoesters most effectively. The cyclic stannoxane can be prepared by heating and refluxing of dibutyltin oxide and ethylene glycol in toluene [68]. The mechanism is similar to a chain-growth polymerization processes. Initiators are thought to operate by Lewis acid activation of the ester group and then transferring a ligand and forming a new ester and an active chain end (Figure 11). Propagation continues until most cyclic oligomers are depleted and the ring-chain equilibration deteriorates. After the polymerization was finished, the authors showed, by using gel permeation chromatography (GPC) that the polymer contained 1-3 % cyclic oligoesters. Figure 12 shows the GPC curves of the cyclic oligomers, the resultant polymer, and commercial PBT. Three major factors that affect polymerization are (1) purity of monomers, (2) good mixing of initiator with oligomers before polymerization, and (3) polymerization at a high rate (polymerization should be completed before crystallization occurred) [45, 57].

MacKnight et al. [57, 68] synthesized ethylene terephthalate cyclic oligomers (ETCs) by the direct synthesis or cyclodepolymerization (ring/chain equilibration) methods, and purified them with several different solvents before the polymerization. They prepared PET by ring opening polymerization with the purified ETCs in the presence of antimony trioxide as a catalyst at 293\(^{\circ}\)C in 15 minutes [57]. The molecular weight of the resultant PETs varied with the preparation and purification methods of ETCs (Table 6). The highest molecular weight
was 25,300 g/mole and it was obtained from the polymerization of ETCs made by direct
synthesis method. They confirmed from HPLC analysis that the ETCs made by the direct
synthesis method has no linear oligomers, unlike those made by the cyclodepolymerization
method (Figure 13). They also stated that the lower the content of the DEG unit in ETCs, the
higher the molecular weight of the resultant PET [57]. The highest molecular weights were
obtained from the ETCs prepared by the direct synthesis method (entry 1 in Table 6) and
purified by THF (entry 5 in Table 6) that have no or a small amount of cyclic oligomers
containing the DEG unit. The ring-opening polymerization was carried out with cyclic
dibutyltin initiator instead of the antimony catalyst [68]. The initiator was prepared by
refluxing dibutyltin oxide and ethylene glycol solution in toluene [68]. The ETCs were
polymerized at 230°C for 10 minutes just after melting at 295°C for 1.5 minutes [68].
Intrinsic viscosity of the resulting PET was 0.5 dL/g [68].
Burch et al. [66] also prepared PET and PET-EI copolymers by ring-opening polymerization
of their cyclic oligomers. They reported that the key variables determining polymerization
rate and molecular weights of the resulting polymer are hydroxyl end groups of linear
oligomer, catalyst level, melting temperature of the cyclic oligomers, polymerization
temperature, and chemical composition of the reaction mixture. The linear oligomers in the
ring-opening polymerization mixture affected the reaction kinetics and can limit the final
molecular weight [66]. Also, the high molecular weight, linear polymers in the ring-opening
polymerization mixture could be used to reduce the melting temperature of the reaction
mixture and the reaction can be carried out at well below the melting temperature for the pure
cyclic oligomers [66]. They created a mixture of cyclic and linear oligo(ethylene
terephthalate) (15 wt %). The mixtures were permitted to react in the melt state at 280°C at 1
atm pressure under nitrogen using 100 ppm titanium catalyst for 1 ~ 120 min. Then each sample was quenched and analyzed for molecular weight and viscosity. Figure 14 shows the results. During the initial, fast polymerization stage, the ring-opening polymerization dominates, with fast disappearance of cyclics conserving the number of reactive linear ends. In the second slower stage, condensation polymerization dominate, involving esterification of residual hydroxyl and carboxyl end groups and transesterification between glycol end groups.

4. PHYSICAL PROPERTIES OF POLYESTERS

Useful properties of PET have spurred numerous studies of other ring-containing polyesters. The characteristics of polyesters depend on structure, symmetry, and conformational features. Table 9 shows melting temperatures of some aromatic phenylene ring-containing polyesters. The terephthalate polyesters are tough, colorless crystalline solids [74]. The glass transition temperatures ($T_g$), property of the amorphous phase, fall steadily with increasing alkylene group content. The members with $x = 3, 4, 6$, or higher even numbers crystallize rapidly from the melt, whereas with $x = 5$ and 7 crystallize slowly [77]. The densities vary with crystallinity, but are in the range of 1.2 – 1.4 g/cm$^3$ [78]. At ambient temperature, the lower members dissolve in relatively few solvents; phenols, phenol-chlorohydrocarbon mixtures, and trihalogenoacetic acids. The poly(alkylene isophthalate)s with meta-substituted rings crystallize only with difficulty and with special techniques [70-72]. Usually crystallization in high polymers with regular repeating units can be achieved by heating the polymer to a temperature above the glass transition temperature or dissolving the polymer and evaporating the solvent. Conix et al. applied both techniques at the same time.
by heating a still-wet film of polymer at temperature slightly above the glass transition temperature of the dry polymer in order to crystallize the series of $m$-phenylene group containing polyesters [70]. Among them, the annealed polyesters of trimethylene glycol and tetramethylene glycol show a more normal spherulitic structure, typical for many crystallized polymers, simply by annealing at 100º C in the oven. In the case of poly(ethylene isophthalate), large and normal spherulites can be grown by crystallization from dichloroethane solution by slow evaporation of the solvent at 60º C. Poly(ethylene isophthalate) melts over a very broad temperature interval and the degrees of crystallization have been relatively low. Table 10 shows the properties of $m$-phenylene group containing polyesters.

Another important property of polyesters is their behavior as gas barrier. PET film is widely used as a packaging material for food, pharmaceuticals, electronics and medical products, because of its good mechanical properties and low cost. However, there is a continuing practical need to improve barrier properties of the PET. Crystallization and orientation are approaches used to obtain barrier enhancement [73-76]. It can also be improved by coating with poly(vinylidene chloride) or vacuum metallization [77]. Copolymerization with other aromatic polyesters with meta- or ortho- phenylene linkage instead of para- linkage is another approach [78-82]. Brolly et al. [83] carried out sorption and diffusion tests with CO$_2$ and PET and PEN films. The results showed that PEN is less permeable than PET and both polymers become less permeable to CO$_2$ when they are oriented [83]. The orientation through drawing or stretching of an amorphous polymer film leads to reorientation and closer chain packing, and restriction of chain mobility. Since sorption and diffusion occur in the amorphous regions, these processes can be altered due to
changes in the spatial distribution of the amorphous phase during drawing. When polymers are stretched, their gas barrier properties improve substantially. It is due to changes in shape, extent and perfection of the non-permeable crystalline regions as well as a result of the ordering effects imparted in the amorphous regions. McGonigle et al. carried out gas transport measurements with several gases, N\textsubscript{2}, Ar, O\textsubscript{2}, CO\textsubscript{2}, and He, for biaxially oriented PET, PEN, and PET-EN copolymers [73]. The permeability coefficient increased in the order N\textsubscript{2} < Ar < O\textsubscript{2} < CO\textsubscript{2} < He [73]. This trend can be expected from the size of the permeant, and the permeability was reduced for the oriented samples. The permeability coefficient of PEN was lower than that of PET, and in the case of copolymer films, the permeability decreased with an increase of PEN content [73]. Table 11 shows permeability coefficients of CO\textsubscript{2} and O\textsubscript{2} for the PET/PEN copolyesters at 30° C.

Polyakova et al. examined the oxygen-barrier properties of amorphous PET based copolymers with various acid comonomers, terephthalate isomers (isophthalate and phthalate inserted kinks and bends in the chain), 3,4’-bibenzoate, 4,4’-bibenzoate, and 2,6-naphthalate (Table 12) [78]. They reported that the incorporation of increasing amounts of isophthalate, phthalate, naphthalate or 3,4’-BB gradually reduced the permeability \( P \) of the polymer film samples (Figure 15 (a)). In contrast, copolymerization with the symmetrical linear isomer, 4,4’-BB, produced a substantial increase in \( P \) (Figure 15a). Changes in diffusivity paralleled change in permeability (Figure 15 b). Kotek et al. compared the diffusion coefficient and permeability of CO\textsubscript{2} gas in PET film with those of PEI film and reported PEI has much better CO\textsubscript{2} barrier property than PET [84]. The collinear attachment of ethylene glycol diester to the phenyl rings in terephthalate and 4,4’-BB units allows for flipping of the phenyl ring. However, due to the non-collinear attachment in isophthalate, phthalate, naphthalate and
3,4’BB units the phenyl ring or naphthyl ring may not be flipped. The flipping of these rings may allow gasses to permeate through, as the gas molecules may use it much like a trap door or valve. These phenyl ring motions have been analyzed [85-88]. Tonelli [87, 88] reported that due to the collinear attachment of ethylene glycol diester residues to the phenyl rings in PET, the terephthaloyl residue is both dynamic and statistical freely rotating link, leading to a potential for phenyl group flipping. However, in the case of PEN, due to the non-collinear attachment of the ethylene glycol residues to naphthyl rings, the PEN chain appears to be less flexible than PET [88]. The ester groups in PEI can rotate independently, but the isophthaloyl unit prevents free rotation [87]. In the case of poly(ethylene phthalate) (PEP), its ester groups may be rotated neither independently nor with low barriers [87].

5. INCLUSION COMPOUNDS BASED ON POLYESTERS AND CYCLODEXTRIN

Cyclodextrins (Figure 16) are cyclic oligosaccharides obtained by enzymatic digestion of starch. They consist of six, seven, and eight glucose units linked by 1,4-α-glucosidic bonds for α-, β-, and γ-cyclodextrin, respectively. Their shallow truncated cone shapes make them act as host molecules for the inclusion of small or long molecule guests. Cyclodextrins are well known as excellent hosts for accepting guest molecules, including aromatic esters [89-91]. The esters may form noncovalent, crystalline inclusion compounds with cyclodextrins as hosts. Packing of the CD molecules within the crystal lattice occurs in one of two principal modes: cage and channel structure (Figure 17) [92]. In the cage structure, both ends of the cavity are blocked by adjacent CDs. CDs usually adopt this cage structure in its crystal hydrates. In the channel structure the CDs are stacked to form endless columns in
the crystal. In polymer-CD inclusion compounds, CD molecules are stacked into columns (channel structure), and the guest polymer chains are included in the CD column channels [93]. Rusa et al. [92] developed a new and easier method for obtaining the channel structure with \( \alpha \)- and \( \gamma \)-CD, containing no guest other than hydration water, and they reported that an appropriate recrystallization process from a suitable solvent under certain conditions leads to the new crystalline form (channel structure).

Bullions et al. [90] produced PET and bisphenol A polycarbonate (PC) samples by the coalescence of their segregated, extended chains from the narrow channels of the crystalline inclusion compounds. The inclusion compounds were formed with the \( \gamma \)-cyclodextrin host and PET and PC guests. Figure 18 shows DSC scans of their PC samples. As-received PC is amorphous with no melting peak. However, the coalesced PC had an endotherm peak around 246\(^\circ\)C. This peak is likely due to the melting of chain-extended PC crystals [90]. In the case of coalesced PET, the degree of crystallinity from the enthalpy of melting was higher than those of as-received PET and solution cast PETs [90]. They reported that the coalesced PC crystallized in a predominantly chain extended morphology, whereas the coalesced PET crystallized in a chain-folded morphology [90]. The polymer-CD inclusion compound technique makes well-mixed blends of two normally immiscible polymers, possible [91, 93]. By simultaneously forming CD inclusion compounds containing two polymers, followed by washing with water to coalesce the guest polymers, intimate blends can be obtained. The homopolymers of PET and PEN are known to be immiscible, and so blending results in a hazy film. The inclusion compound in which the \( \gamma \)-cyclodextrin channel structure simultaneously hosted PET and PEN was formed, and then the coalescence of the polymers from the inclusion compounds resulted in a blend with well-mixed amorphous regions [91].
Based on the literature review, it appears that the novel manufacturing method, namely the ring-opening polymerization (ROP) of cyclic oligoesters, has a lot of advantages over the conventional polymerization method. A number of aromatic polyesters have been synthesized by using this new method under atmospheric pressures in shorter polymerization times [63-69]. However, there has been no research reported to examine this new technique for making fiber-forming polyesters. Fiber-forming quality polyesters should not contain too much cyclic oligomers, because the cyclic oligomers interrupt the spinning process [94]. Among the aromatic polyesters, poly(ethylene terephthalate) (PET) is the predominant commercial fiber-forming polyester. Poly(trimethylene terephthalate) (PTT) is a relatively new polymer. It was commercialized a few years ago and it has a great potential to become a major polyester for making fibers. Poly(ethylene isophthalate) (PEI) and poly(trimethylene isophthalate) (PTI) are the structural isomers of PET and PTT, respectively, containing phenyl rings with carboxyl groups attached in the meta position (1,3) [70, 71, 84]. Because of their noncollinear chain structures (meta linkage), these isophthalic acid based amorphous polyesters may have lower permeabilities than terephthalic acid based polyesters (PET and PTT) [84, 86, 87]. Their chemical structures are as follows;

\[
\text{PET} \quad \text{HO}-[\cdot \text{CO} \hspace{1cm} \text{OCO} \hspace{1cm} \text{CH}_2\text{CH}_2\text{O}]_n-\text{H} \\
\text{PTT} \quad \text{HO}-[\cdot \text{CO} \hspace{1cm} \text{OCO} \hspace{1cm} \text{CH}_2\text{CH}_2\text{O}]_n-\text{H}
\]
First, we propose to make these four polyesters using a 1-gallon Parr reactor using the conventional method (condensation polymerization). As shown in Figures 19 and 20 this is a two-step process that involves the esterification of terephthalic or isophthalic acid with a diol and the subsequent polycondensation. The manufactured polyesters will be characterized as-synthesized and in film or fiber forms in order to examine their potential as commercial film or fiber products.

The major disadvantage of the conventional polymerization method for PET is a long polymerization time. It takes around 5 hours to complete the first step and 5 hours for the 2nd polycondensation step. Furthermore, a very low pressure of less than 1 Torr is needed in order to remove low molecular weight by-product. However, the non-conventional method, ring-opening polymerization (ROP), does not produce any by-products, so it does not require low pressure [63-69]. Also the reaction time is very short, compared with the conventional method [63-69]. So, we propose to prepare these polyesters by ROP and to investigate whether the ring-opening polymerization of cyclic oligoesters, is a useful manufacturing method for making fiber-forming polyesters. There is no research reported on the synthesis of fiber-forming quality polyesters by ROP. The synthesis of the isophthalic acid based polyesters by ROP has also not been investigated. We propose the cyclo-depolymerization (CDP) method for the preparation of the cyclic oligoesters as feedstock for the ROP. This
technique is useful for recycling of polyesters [50-55, 57]. A typical CDP is carried out by refluxing in dilute solution for many hours in the presence of metal catalysts such as organotin or titanate compound [50-55, 57]. A high purity PTT cyclic dimer, which is usually collected in a conventional PTT manufacturing plant as a by-product, will be also used as a raw material for ROP. The ROP will be carried out with several different catalysts at several different concentrations. There has been no research done on ROP with cyclics produced during conventional manufacturing or on how catalyst concentration affects the conversion to fiber-forming polyesters. Figures 19 and 20 show the schematic representations of conventional polymerization and ring-opening polymerization.

One of the most important properties of PET is its gas barrier property. PET has been used as a packaging material worldwide for a long time because of its good mechanical properties and low cost. However, there is a continuing practical need to improve barrier properties of PET [73-83]. Isophthalic acid based polyesters, such as PEI, may potentially substitute for PET film in applications where PET would not suffice [84]. We propose to examine the diffusion coefficient, solubility and permeability of CO₂ in amorphous PEI and PET films by a gas sorption method.

Because of its kinked chemical structure PEI is almost a totally amorphous polyester [70-71]. It has been reported that coalescence from polymer-cyclodextrin inclusion compounds can reorganize morphologies and conformations of the guest polymers and sometimes improve their crystallizability [90]. We propose to improve the orientation of PEI chains and crystallizability through coalescence from PEI / γ-CD inclusion compounds (ICs).
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Table 1. Raw materials for the manufacturing of different polyesters

<table>
<thead>
<tr>
<th>Polyesters</th>
<th>Transesterification method</th>
<th>Direct esterification method</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>Ethylene glycol Dimethyl terephthalate</td>
<td>Ethylene glycol Terephthalic acid</td>
</tr>
<tr>
<td>PTT</td>
<td>1,3-Propanediol Dimethyl terephthalate</td>
<td>1,3-Propanediol Terephthalic acid</td>
</tr>
<tr>
<td>PBT</td>
<td>1,4-Butanediol Dimethyl terephthalate</td>
<td>1,4-Butanediol Terephthalic acid</td>
</tr>
<tr>
<td>PEN</td>
<td>Ethylene glycol Dimethyl naphthalate</td>
<td>Ethylene glycol 2,6-naphthalene-dicarboxylic acid</td>
</tr>
<tr>
<td>PEI</td>
<td>Ethylene glycol Dimethyl isophthalate</td>
<td>Ethylene glycol Isophthalic acid</td>
</tr>
<tr>
<td>PTI</td>
<td>1,3-Propanediol Dimethyl isophthalate</td>
<td>1,3-Propanediol Isophthalic acid</td>
</tr>
<tr>
<td>PBI</td>
<td>1,4-Butanediol Dimethyl isophthalate</td>
<td>1,4-Butanediol Isophthalic acid</td>
</tr>
</tbody>
</table>
Table 2. Intrinsic viscosity, esterification time, and molecular weight of PTT samples [28]

<table>
<thead>
<tr>
<th>Esterification catalyst</th>
<th>Polycondensation catalyst</th>
<th>I. V. (dl/g)</th>
<th>Esterification time (min)</th>
<th>$M_W$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No catalyst</td>
<td>No catalyst</td>
<td>0.36</td>
<td>1060</td>
<td>12,510</td>
</tr>
<tr>
<td>Zn-acetate</td>
<td>Sb$_2$O$_3$</td>
<td>0.16</td>
<td>600</td>
<td>3,860</td>
</tr>
<tr>
<td>Ti(OC$_4$H$_9$)$_4$</td>
<td>Sb$_2$O$_3$</td>
<td>0.64</td>
<td>230</td>
<td>28,800</td>
</tr>
<tr>
<td>Ti(OC$_4$H$_9$)$_4$</td>
<td>Ti(OC$_4$H$_9$)$_4$</td>
<td>0.74</td>
<td>215</td>
<td>35,550</td>
</tr>
<tr>
<td>Ti(OC$_4$H$_9$)$_4$+Zr(OC$_4$H$_9$)$_4$</td>
<td>Sb$_2$O$_3$</td>
<td>0.69</td>
<td>240</td>
<td>32,120</td>
</tr>
</tbody>
</table>
Table 3. Isolation of individual compounds from total dioxane extract of poly(ethylene terephthalate) [39]
Table 4. Cyclic oligomers of poly(ethylene terephthalate) [40]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Identification</th>
<th>Mp (°C)</th>
<th>Molecular weight</th>
<th>DEG/TPA ratio</th>
<th>Composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
<td>Theory</td>
<td>Found</td>
</tr>
<tr>
<td>α</td>
<td>Cyclic trimer</td>
<td>319</td>
<td>600</td>
<td>576.5</td>
<td>0.00</td>
</tr>
<tr>
<td>β</td>
<td>Cyclic tetramer</td>
<td>326</td>
<td>768.7</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>γ</td>
<td>Cyclic pentamer with DEG</td>
<td>190</td>
<td>0.2</td>
<td>0.2</td>
<td>6.7</td>
</tr>
<tr>
<td>δ</td>
<td>Cyclic pentamer</td>
<td>256</td>
<td>900</td>
<td>960.9</td>
<td>0.00</td>
</tr>
<tr>
<td>ε</td>
<td></td>
<td>304</td>
<td></td>
<td>0.08</td>
<td>10.6</td>
</tr>
<tr>
<td>ζ</td>
<td></td>
<td></td>
<td></td>
<td>0.18</td>
<td>4.6</td>
</tr>
<tr>
<td>η</td>
<td></td>
<td>185</td>
<td>1730</td>
<td>0.11</td>
<td>17.4</td>
</tr>
<tr>
<td>θ</td>
<td>185-190a</td>
<td>1590</td>
<td>0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cyclic dimer</td>
<td>175, 224b</td>
<td>420</td>
<td>384</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*a* No sharp melting point, just a broad endotherm with an exotherm starting at 200 °C.

*b* Two sharp melting points indicated by DTA.
Table 5. Solvents and catalysts for cyclo-depolymerization reactions.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Conc. of polymer</th>
<th>Catalyst</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(tetraethylene isophthalate)</td>
<td>Chlorobenzene</td>
<td>1/100 (w/w), 1/30 (w/w)</td>
<td>Dibutyltin oxide</td>
<td>50</td>
</tr>
<tr>
<td>Poly(tetraethylene terephthalate)</td>
<td>Chlorobenzene</td>
<td>1/100 (w/w), 1/30 (w/w)</td>
<td>Dibutyltin oxide</td>
<td>50</td>
</tr>
<tr>
<td>Poly(tetraethylene orthophthalate)</td>
<td>Chlorobenzene</td>
<td>1/100 (w/w)</td>
<td>Dibutyltin oxide</td>
<td>50</td>
</tr>
<tr>
<td>Poly(decamethylene terephthalate)</td>
<td>Chlorobenzene</td>
<td>1/100 (w/w)</td>
<td>Dibutyltin oxide</td>
<td>50</td>
</tr>
<tr>
<td>Poly(decamethylene isophthalate)</td>
<td>Chlorobenzene</td>
<td>1/100 (w/w)</td>
<td>Dibutyltin oxide</td>
<td>50</td>
</tr>
<tr>
<td>Poly(decamethylene orthophthalate)</td>
<td>Chlorobenzene</td>
<td>1/100 (w/w)</td>
<td>Dibutyltin oxide</td>
<td>50</td>
</tr>
<tr>
<td>Poly(ethylene isophthalate)</td>
<td>Chlorobenzene</td>
<td>1.25 % (w/v)</td>
<td>dibutyltin oxide</td>
<td>51</td>
</tr>
<tr>
<td>Poly(tetraethylene isophthalate)</td>
<td>Chlorobenzene</td>
<td>1.25 % (w/v)</td>
<td>dibutyltin oxide</td>
<td>51</td>
</tr>
<tr>
<td>Poly(hexamethylene isophthalate)</td>
<td>Chlorobenzene, 1,2-dichlorobenzene</td>
<td>1 % (w/v), 2 % (w/v)</td>
<td>dibutyltin oxide</td>
<td>51</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>1,2-dichlorobenzene</td>
<td>1/100 (w/v)</td>
<td>dibutyltin oxide</td>
<td>52</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>1-methyl naphthalene</td>
<td>1/10 (w/w), 1/20 (w/w), 1/30 (w/w)</td>
<td>Tetraisopropyl orthotitanate, Dibutyltin bis(2-ethyl-hexanoate), zinc acetate</td>
<td>53</td>
</tr>
<tr>
<td>Poly(butylene terephthalate)</td>
<td>1,2-dichlorobenzene</td>
<td>1/10 (w/v)</td>
<td>Dibutyltin oxide</td>
<td>54</td>
</tr>
<tr>
<td>Poly(butylene terephthalate)</td>
<td>1,2-dichlorobenzene</td>
<td>0.05 - 0.2 M</td>
<td>Cyclic stannoxane</td>
<td>55</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>1,2-dichlorobenzene</td>
<td>0.05 M</td>
<td>Titanate catalyst</td>
<td>57</td>
</tr>
</tbody>
</table>
Table 6. Molecular weight of PET polymerized from various ETCs with 0.5 mol % antimony(III) oxide at 293° C for 15 minutes [57]

<table>
<thead>
<tr>
<th>entry</th>
<th>ETCs</th>
<th>Yield (wt %)</th>
<th>Cyclics%</th>
<th>Trimer in ETCs%</th>
<th>DEG unit (mol %)</th>
<th>IV (dL/g)</th>
<th>$M_n$</th>
<th>Polymer color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Direct synthesis method</td>
<td>99.9</td>
<td>57.0</td>
<td></td>
<td></td>
<td>0.61</td>
<td>25 300</td>
<td>White</td>
</tr>
<tr>
<td>2</td>
<td>Soluble in DCM(a)</td>
<td>92</td>
<td>92.7</td>
<td>52.1</td>
<td>0.46</td>
<td>17 200</td>
<td>Gray</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Soluble in dioxane(a)</td>
<td>96</td>
<td>97.4</td>
<td>46.2</td>
<td>0.46</td>
<td>17 200</td>
<td>Gray</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Soluble in DCM, Insoluble in acetone(a)</td>
<td>61</td>
<td>94.2</td>
<td>38.6</td>
<td>0.47</td>
<td>17 700</td>
<td>Gray</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Soluble in DCM, Insoluble in THF(a)</td>
<td>28</td>
<td>98.8</td>
<td>33.0</td>
<td>1.8</td>
<td>0.60</td>
<td>24 800</td>
<td>White</td>
</tr>
<tr>
<td>6</td>
<td>Soluble in DCM, soluble in THF(a)</td>
<td>72</td>
<td>91.0</td>
<td>32.1</td>
<td>5.9</td>
<td>0.34</td>
<td>11 400</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

\(a\) Cyclodepolymerization. \(b\) From HPLC peak area. \(c\) From NMR.

DCM: dichloromethane, THF: tetrahydrofuran
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Preparation method for cyclics</th>
<th>Reaction Temp. (°C)</th>
<th>Reaction Time (min)</th>
<th>Catalyst (or initiator)</th>
<th>Highest molecular-weight</th>
<th>Ref#</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBT</td>
<td>Pseudo-high dilution</td>
<td>190</td>
<td>20</td>
<td>Cyclic stannoxane, tetrakis(2-ethylhexyl)-titanate</td>
<td>445,000(^a) g/mol</td>
<td>45</td>
</tr>
<tr>
<td>P(BT-ε-caprolactone)(^d)</td>
<td>Cyclo-depolymerization</td>
<td>190</td>
<td>15</td>
<td>Fomrez SUL-11A (dibutyltin dioxide / DIOP plasticizer, 1/1)</td>
<td>140,000(^a) g/mol</td>
<td>67</td>
</tr>
<tr>
<td>PET</td>
<td>Cyclo-depolymerization / high dilution</td>
<td>293</td>
<td>10 ~ 15</td>
<td>Antimony trioxide</td>
<td>32,100(^b) g/mol</td>
<td>57</td>
</tr>
<tr>
<td>PET</td>
<td>Cyclo-depolymerization / high dilution</td>
<td>285</td>
<td>10</td>
<td>Titanium(IV) isopropoxide</td>
<td>38,900(^a) g/mol</td>
<td>66</td>
</tr>
<tr>
<td>PET</td>
<td>Cyclo-depolymerization</td>
<td>230</td>
<td>10</td>
<td>Cyclic stannoxane</td>
<td>0.51(^c) dL/g</td>
<td>68</td>
</tr>
<tr>
<td>PTT</td>
<td>Cyclo-depolymerization</td>
<td>300</td>
<td>120</td>
<td>Dibutyltin oxide</td>
<td>0.66(^c) dL/g</td>
<td>53</td>
</tr>
<tr>
<td>PBN / PEN</td>
<td>Direct synthesis</td>
<td>275 / 295-300</td>
<td>15 / 25</td>
<td>Dibutyltin oxide / Titanium (IV) propoxide</td>
<td>0.28(^c) dL/g 0.24(^c) dL/g</td>
<td>65</td>
</tr>
<tr>
<td>PEN / PET-EN copolymer</td>
<td>Cyclo-depolymerization</td>
<td>320-365</td>
<td>5</td>
<td>Antimony trioxide</td>
<td>0.42(^c) dL/g 0.37(^c) dL/g</td>
<td>69</td>
</tr>
</tbody>
</table>

\(^a\) weight average molecular weight  
\(^b\) number average molecular weight  
\(^c\) intrinsic viscosity  
\(^d\) obtained by co-polymerization of cyclic oligoester CBT with ε-caprolactone
Table 8. Polymerization of macrocyclic ethylene terephthalate dimer with various catalysts [43]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conc. of Catalyst (mol %)</th>
<th>Temp. (°C)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Time (min)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Conv. (%)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
<td>300</td>
<td>20</td>
<td>19</td>
<td>11,800</td>
<td>Yellow</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>222</td>
<td>480</td>
<td>34</td>
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<td></td>
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<td>300</td>
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<td>0.4</td>
<td>222</td>
<td>240</td>
<td>26</td>
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<td>Colorless</td>
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<td></td>
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<td>300</td>
<td>20</td>
<td>87</td>
<td>14,700</td>
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<td>0.4</td>
<td>222</td>
<td>120</td>
<td>14</td>
<td>4,800</td>
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<td>222</td>
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<td>98</td>
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<td>60</td>
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<td>88</td>
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<td></td>
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<td>98</td>
<td>16,000</td>
<td>Brown</td>
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<td>96</td>
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<td>222</td>
<td>240</td>
<td>64</td>
<td>44,500</td>
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<td>4</td>
<td>275</td>
<td>120</td>
<td>96</td>
<td>14,700</td>
<td>Yellow</td>
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<td>0.04</td>
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<td>19</td>
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<td>0.4</td>
<td>222</td>
<td>240</td>
<td>64</td>
<td>44,500</td>
<td>Colorless</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>275</td>
<td>120</td>
<td>96</td>
<td>14,700</td>
<td>Yellow</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>222</td>
<td>60</td>
<td>19</td>
<td>6,200</td>
<td>Colorless</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>222</td>
<td>20</td>
<td>91</td>
<td>24,800</td>
<td>Colorless</td>
</tr>
<tr>
<td></td>
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<td>222</td>
<td>5</td>
<td>100</td>
<td>22,900</td>
<td>Colorless</td>
</tr>
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<td></td>
<td>4</td>
<td>200</td>
<td>3</td>
<td>100</td>
<td>36,100</td>
<td>Colorless</td>
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<td>4</td>
<td>175</td>
<td>60</td>
<td>87</td>
<td>22,000</td>
<td>Colorless</td>
</tr>
</tbody>
</table>

<sup>a</sup> Heating rate of 10° C/min.
<sup>b</sup> The heating time was recorded from the point when the reaction temperature was attained.
<sup>c</sup> Estimated by SEC (based on polystyrene standards).
<sup>d</sup> 1,3-dichloro-1,1,3,3-tetraphydristannoxane has a dimeric ladder structure induced by coordination of oxygen to tin in the other chain.
Table 9. Transition temperatures of ring-containing polyesters [77]

<table>
<thead>
<tr>
<th>Series</th>
<th>Structural type</th>
<th>Repeating-unit formula</th>
<th>$T_m$ °C, for repeating unit with $x$=</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Poly(alkylene terephthalate)</td>
<td>$\text{-O(CH}_2\text{)}_x\text{-CO-CO-}$</td>
<td>269 265 233 232 134 154 85 132 95 125</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_g^a$</td>
<td>115 95 80 45 45 45 35 25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_g^b$</td>
<td>101 69 35 22 10 -9 3 -3 -5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Poly(alkylene isophthalate)</td>
<td>$\text{-O(CH}_2\text{)}_2\text{-CO-CO-}$</td>
<td>240 132 152 am 140</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Poly(alkylene 4,4'-bibenzoate)</td>
<td>$\text{-O(CH}_2\text{)}_x\text{-CO-CO-}$</td>
<td>350 280 328 217 240 150 193 128 164</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Poly(alkylene 2,6-naphthalene-dicarboxylate)</td>
<td>$\text{-O(CH}_2\text{)}_x\text{-CO-CO-}$</td>
<td>340 266 199 241 135 211 130 185 124 144</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

$^a$ Values reported by dynamic mechanical testing methods

$^b$ Values reported by thermal analysis methods
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Crystalline melting point (°C)</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ethylene isophthalate)</td>
<td>240</td>
<td>Softens at 110° C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Density (amorphous) = 1.346 g/cm³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Density (crystalline) = 1.358 g/cm³</td>
</tr>
<tr>
<td>Poly(trimethylene isophthalate)</td>
<td>132</td>
<td>Softens at 80° C, fibers show “cold drawing”</td>
</tr>
<tr>
<td>Poly(tetramethylene isophthalate)</td>
<td>152</td>
<td>Softens at 85° C, fibers show “cold drawing”</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Density (amorphous) = 1.268 g/cm³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Density (crystalline) = 1.309 g/cm³</td>
</tr>
<tr>
<td>Poly(pentamethylene isophthalate)</td>
<td>-</td>
<td>Rubbery, softens at about 100° C, does not crystallize</td>
</tr>
<tr>
<td>Poly(hexamethylene isophthalate)</td>
<td>140</td>
<td>Rubbery, softens at about 150° C</td>
</tr>
</tbody>
</table>
Table 11. Permeability coefficients of oxygen and CO$_2$ for the PET/PEN polyesters at 30\(^\circ\) C [73]

<table>
<thead>
<tr>
<th>Material</th>
<th>Draw area$^a$</th>
<th>Gas</th>
<th>$P \times 10^{13}$ ($\text{cm}^3 \ (\text{STP})\text{cm}$)</th>
<th>($\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>6.8</td>
<td>O$_2$</td>
<td></td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>12.8</td>
<td></td>
<td></td>
<td>31</td>
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<tr>
<td>PETN8$^c$</td>
<td>6.8</td>
<td></td>
<td></td>
<td>35</td>
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<tr>
<td></td>
<td>12.2</td>
<td></td>
<td></td>
<td>29</td>
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<tr>
<td>PETN16$^d$</td>
<td>7.0</td>
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<td></td>
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<tr>
<td></td>
<td>13.6</td>
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<td></td>
<td>26</td>
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<tr>
<td>PETN84$^e$</td>
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<td></td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td>12.0</td>
<td></td>
<td></td>
<td>9.0</td>
</tr>
<tr>
<td>PEN</td>
<td>8.4</td>
<td></td>
<td></td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>12.2</td>
<td></td>
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<td>7.5</td>
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<tr>
<td>PET</td>
<td>CA$^b$</td>
<td>CO$_2$</td>
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<td>173</td>
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<td>12.8</td>
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<td>178</td>
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<td>178</td>
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<tr>
<td></td>
<td>12.2</td>
<td></td>
<td></td>
<td>177</td>
</tr>
<tr>
<td>PETN16</td>
<td>CA</td>
<td></td>
<td></td>
<td>71</td>
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<tr>
<td></td>
<td>7.0</td>
<td></td>
<td></td>
<td>145</td>
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<tr>
<td></td>
<td>13.6</td>
<td></td>
<td></td>
<td>131</td>
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<tr>
<td>PETN84</td>
<td>10.5</td>
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<td></td>
<td>43</td>
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<tr>
<td>PEN</td>
<td>8.4</td>
<td></td>
<td></td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>12.2</td>
<td></td>
<td></td>
<td>22</td>
</tr>
</tbody>
</table>

$^a$ Draw area = (machine direction ratio) x (transverse direction ratio)

$^b$ CA refers to the original cast amorphous sheet.

$^c$ PETN8: copolymer with ET 92% and EN 8%

$^d$ PETN16: copolymer with ET 84% and EN 16%

$^e$ PETN84: copolymer with ET 16% and EN 84%
Table 12. Structure and designation of acid repeat units for PET-based copolymers [78]

<table>
<thead>
<tr>
<th>Structure</th>
<th>Designation</th>
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</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure" /></td>
<td>Terephthalate (T)</td>
</tr>
<tr>
<td><img src="image2" alt="Structure" /></td>
<td>Isophthalate (I)</td>
</tr>
<tr>
<td><img src="image3" alt="Structure" /></td>
<td>Phthalate (P)</td>
</tr>
<tr>
<td><img src="image4" alt="Structure" /></td>
<td>3,4′- Bibenzoate (3,4′BB)</td>
</tr>
<tr>
<td><img src="image5" alt="Structure" /></td>
<td>4,4′- Bibenzoate (4,4′BB)</td>
</tr>
<tr>
<td><img src="image6" alt="Structure" /></td>
<td>Naphthalate (N)</td>
</tr>
</tbody>
</table>
Figure 1. Schemes for the PET polymerization process
Figure 2. Mechanisms of catalysis in polycondensation reaction [29]
Figure 3. The main cyclic oligomers from PET, PEI and PET-PEI copolymer [42]
Figure 4. The chemical structures of compounds A, B, C, and D extracted from the PET chip and fiber [39]
Figure 5. Preparation of butylene terephthalate cyclic oligomers by (a) pseudo-high dilution method and (b) classical high dilution method [45]
Figure 6. Schematic representation of the polymer-supported synthesis of cyclic oligoester [49]
Figure 7. Synthesis of linear poly(alkyldene isophthalate)s and the cyclo-depolymerization of these polymers. \( Q^+ \) is the quaternary ammonium cation, i.e. tetra-\( n\)-butylammonium [51].
Figure 8. GPC traces of cyclic oligo(ethylene terephthalate), where $x = 3$–$8$, from an extraction of chip with mixed xylene isomers and solution ring chain reactions with zinc acetate as catalyst at polymer/solvent dilution ratios of 1/10, 1/20, and 1/30 [53].
Figure 9. Conversion of monomers to low viscosity macrocyclics (bottom) allows processing and polymerization to be carried out simultaneously. Conventional polymerization (top) forms viscous polymers which may be difficult to process [44]
Figure 10. Chemical structure of stannoxane initiator for ring-opening polymerization of cyclic oligoesters [45]
Figure 11. Polymerization of poly(butylene terephthalate) cyclics via ring-opening utilizing titanium alkoxide catalysis: Initiation and propagation steps [45]
Figure 12. GPC traces of (a) PBT cyclic oligomers, (b) polymer resulting from polymerization of cycles, and (c) commercial PBT (Valox 315) [45]
Figure 13. HPLC trace of various ETCs in Table 6 for analysis of linear oligomers; (1) prepared by direct synthesis method, (2) prepared by cyclodopolymerization, the part soluble in dichloromethane (DCM), (3) prepared by cyclodopolymerization, the part soluble in dioxane, (4) prepared by cyclodepolymerization, the part soluble in DCM and insoluble in acetone, (5) prepared by cyclodepolymerization, the part soluble in DCM and insoluble in tetrahydrofuran (THF) [57]
Figure 14. Typical two stage polymerization behavior observed for cyclic oligo(ethylene terephthalate) polymerizations, showing rapid polymerization by ring-opening of the cyclic oligomer followed by slower, diffusion-limited, polycondensation [66]
Figure 15. Effect of copolymer composition on (a) logarithm of oxygen permeability and (b) logarithm of oxygen diffusivity [78]
Chemical structure of α-CD

Figure 16. Structure and molecular dimensions of α-, β-, γ-cyclodextrins (CD)
Figure 17. Schematic representation of the packing of cyclodextrin molecules within their crystals. In the channel structure, CD molecules form a lattice: channel structure (a), cage herringbone type (b), and cage brick type (c) [92]
Figure 18. DSC scans of (a) IC-coalesced bisphenol A polycarbonate (PC) run I, (b) IC-coalesced PC run II, (c) solution-cast PC run I, (d) solution-cast PC run II, and (e) as-received PC [90]
Figure 19. Schematic representation for (a) the conventional polymerization and (b) ring opening polymerization of PET and PTT
Figure 20. Schematic representation for (a) the conventional polymerization and (b) ring opening polymerization of PEI and PTI
CHAPTER 2. SYNTHESIS, MELT SPINNING AND CHARACTERIZATION OF CONVENTIONALLY MANUFACTURED POLYESTERS

1. INTRODUCTION

Linear polyesters were first synthesized by Carothers and coworkers. The fiber drawn from the molten polyester of trimethylene glycol and hexadecamethylene dicarboxylic acid was the first synthetic fiber. However, it had a low melting point and poor hydrolytic stability. Later Whinfield and Dickson discovered poly(ethylene terephthalate) (PET), which was high melting (265°C) temperature and had good hydrolytic stability. Subsequently many other aromatic polyesters have been studied. Among these polyesters, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) have been produced commercially for more than 50 years. Poly(trimethylene terephthalate) (PTT) was commercialized very recently. PET is used world wide for the production of synthetic fibers, films, beverage bottles, and molded plastic parts, because of its good physical properties. The structural isomers of PET and PTT, poly(ethylene isophthalate) (PEI) and poly(trimethylene isophthalate) (PTI) are relatively unexplored polymers.
In this chapter, the polyesters, PET, PTT, PEI, and PTI were manufactured in 1-gallon Parr reactor and melt-spun with several take-up speeds. Thermal and mechanical properties of the polymers and fibers are reported.

2. EXPERIMENTS

2.1. Materials

Dimethyl terephthalate, ethylene glycol, and 1,3-propandiol were supplied by DuPont. Isophthalic acid and terephthalic acid were supplied by Amoco. Zinc acetate, antimony trioxide, titanium butoxide, phenol, and 1,1,2,2-tetrachloroethane (TCE) were all obtained from Aldrich.

2.2. Polymer synthesis

The polymerization was carried out in a 1-galon reactor (Parr) equipped with vacuum pump, condenser, and cold trap for collecting by-product. The typical recipes are shown in Table 1. The synthesis was carried out in two different steps. Diacid or diester and diol in a molar ratio of 1 / 2.5 and the catalysts, 5x10^{-4} mol/mol diacid (or diester) of zinc acetate and 5x10^{-4} mol/mol diacid (or diester) of antimony trioxide, or 5x10^{-4} mol/mol diacid (or diester) of titanium butoxide, and 500 ppm of trimethyl phosphate were added to the Parr reactor. In the
first step, the esterification reaction was conducted at the desired reaction temperature under nitrogen atmosphere. The reaction mixture was stirred at a constant speed. During the reaction, water was distilled and collected as a byproduct. In the second step (polycondensation), the oligomers, made in the first step, were gradually heated to the desired reaction temperature. Vacuum was applied after reaching the reaction temperature and the pressure was slowly reduced to 0.4 ~ 0.6 torr over 30 minutes. During the reaction, ethylene glycol or propanediol was collected in a cold trap. The reaction was stopped when the stirring torque increased no more. The product was extruded through the drain valve and chopped in a polymer chopper.

2.3. Melt spinning

The synthesized polyesters were dried at the desired temperature under vacuum overnight. The temperature was 130° C for PET and PTT, and 45° C for PEI and PTI, because PEI and PTT have low softening temperatures. The spinning was carried out with a Fourne single screw extruder with a diameter of 22 mm for PET and PTT and the Bradford piston type spinning machine for PEI and PTI. The round orifice of spinneret plate was 0.6 mm in diameter and 1.38 mm in length. Take-up speeds varied from 2000 to 5000 m/min.
2.4. Intrinsic Viscosity and molecular weight measurement

Intrinsic viscosity was measured by using an Ubbelohde viscometer in a water bath thermostated at 25°C. The solvent was a mixture of phenol and 1,1,2,2-tetrachloroethane with 60/40 weight ratio. The intrinsic viscosity was estimated from the single-point method, Billmeyer method [1]. The following equation was used:

\[
V_{\text{int}} = \frac{1}{4} V_{\text{red}} + \frac{3 \ln V_{\text{rel}}}{4C},
\]

where \( V_{\text{int}} \): intrinsic viscosity, \( V_{\text{red}} \): reduced viscosity \( = \frac{V_{\text{rel}} - 1}{C} \), \( V_{\text{rel}} \): relative viscosity = (flow time of solution/flow time of solvent).

The number-average molecular weights were obtained from the following the Mark-Houwink relations [2].

For PET

\[
[\eta] = 7.61 \times 10^{-4} M_n^{0.67},
\]

for PTT

\[
[\eta] = 8.20 \times 10^{-4} M_n^{0.63},
\]

and for PEI

\[
[\eta] = 8.15 \times 10^{-4} M_n^{0.645}.
\]
In the case of PTI, K and $\alpha$ have not been reported, so its molecular weight could not be measured, and only the intrinsic viscosity is reported in this chapter.

2.5. Differential Scanning Calorimetry (DSC) analyses

DSC measurements were conducted on a Perkin-Elmer™ Differential Scanning Calorimeter (DSC-7). During the measurements, N$_2$ gas was purged at a constant flow rate. Indium was used as a calibration standard. The scanning rates of 20° C/ min were used.

2.6. Thermogravimetric Analysis (TGA)

TGA measurements were conducted on a Perkin-Elmer Pyris 1 TGA Thermogravimetric Analyzer. During the measurements, N$_2$ gas was purged at a constant flow rate. The heating rates for all samples were 20° C/ min.

3. RESULTS AND DISCUSSION

3.1. Polymerization

Four polyesters PET, PTT, PEI, and PTI were synthesized in 1-galon Parr reactor by using condensation polymerization method. During the polymerization water or methanol and ethylene glycol or propanediol were produced as a byproduct in the 1$^{st}$ and 2$^{nd}$ step,
respectively. In order to calculate the reaction conversions the amounts of by-products were carefully determined. The first step (direct esterification or transesterification) reaction was stopped when the conversions reached almost 100% (no more water or methanol came out). During the polycondensation step under high vacuum (0.4–0.6 torr), the stirring torque increase was monitored. The polycondensation reaction step was stopped when there was no further change in stirring torque. Figure 1 shows the torque change during the polymerization for all the polyesters. The slope of the curve for PET was the highest and that of PEI was the lowest. The reaction kinetics of PET and PTT were almost the same (PET has a little bit faster kinetics). The isophthalate polyesters (PEI and PTI) show much slower kinetics than terephthalate polyesters (PET and PTT).

The reaction conversions, calculated by the amount of diols produced during the polymerization step are shown in Table 2. Table 2 also shows the intrinsic viscosity and molecular weight for these polyesters. The reaction conversion varied from 70 to 88% for each polymer. The intrinsic viscosity and number average molecular weight were 0.45–0.58 dL/g and around 18000–33000 g/mol, respectively.

3.2. Polymer Thermal Properties

Figure 2 shows DSC curves measured for the polyesters synthesized in the Parr reactor. PET
and PTT show glass transition (Tg), cold crystallization (Tcc), and melting peak (Tm) at 71, 144, and 253, and 48, 69, and 228 °C, respectively. PEI shows Tg, Tcc, and Tm at 54, 176, and 243 °C, but the heats of crystallization fusion are very small. Thus indicating that the polymer is nearly amorphous and it has very a small degree of crystallinity. PTI does not have Tcc or Tm. As-synthesized PTI was originally an amorphous material and did not crystallize during heating at 20° C/min in the DSC. The PEI and PTI show only Tg at 54 and 43° C, respectively. This might be because their kinked chain structure (caused by meta linkage of ester to phenyl ring) prevents chain folding for crystallization.

PET has the highest Tg at 71° C and PTI has the lowest Tg at 43° C. But the Tg’s for PTT, PEI, and PTI were not much different. Because of the low Tg, PTT, PEI, and PTI might be softer and more rubbery materials than PET that has a much higher Tg and is a stiffer material. These low-Tg-polyesters can be used to overcome some disadvantages of PET caused by its high Tg. We can expect that copolymers of low-Tg-polyesters and PET may have a lower glass transition temperature make processes, like dyeing or molding, much easier. In the case of the amorphous polyesters, PEI and PTI can be used to prevent crystallization of PET or improve the clarity of PET bottles.

Table 3 shows the DSC data from the PEI obtained from polymerization in the Parr reactor and the small-scale reaction tube (see Chapter 2), and PEI crystallized by different methods.
While the PEI prepared in the small polymerization tube (lab-PEI) has no Tcc and Tm at all, the PEI prepared in the Parr reactor (Parr-PEI) has melting temperature at around 242° C. This is because in the case of Parr-PEI, the polymer melt was extruded through the drain valve of the reactor. It is possible that during that extrusion PEI chains got oriented and the polymer crystallized. As-synthesized Parr-PEI, annealed PEI, and melt-casted PEI show their melting temperature at 242~244° C with a very small heat of fusion (4 ~ 6 J/g). However, a solution-casted sample shows very low melting temperature (124° C) with a relatively high crystallinity (the heat of fusion of 27 J/g). There have been contrary results reported about the melting temperature of PEI [3-8]. Some researchers reported that PEI melts at 230~240° C with small heats of fusion, 1.4 ~ 2.4 J/g [3-6]. But some researchers [7, 8] reported that the melting point of PEI is 130~140° C with larger heat of fusion (30.6 J/g), and also they pointed out that the result of high melting temperature might be due to the cyclic dimer of ethylene isophthalate that remained in the polymer. Our results show solution-cast PEI crystalline has a low melting point, and melt-extruded PEI and melt-cast PEI film have high melting points. PEI might form different kinds of crystals depending on the type of crystallization method; the crystals formed by annealing have a high melting temperature and the ones formed by solution casting have a low melting temperature. The crystallization rate for PEI is perhaps higher for the solution-cast method than by the annealing method.
Figure 3 shows TGA curves for the commercial and conventionally synthesized polyesters. The polyesters were thermally degraded over the range of 400 $\sim$ 500 $^\circ$ C. Table 4 shows the degradation temperatures obtained from the TGA curves. Based on these results it can be concluded that the thermal stability of the polyesters can be given in the descending order as follows:

$$\text{PET} > \text{PEI} > \text{PTT} > \text{PTI}.$$ 

### 3.3. Fiber Characterization

The synthesized PET and PTT were melt-spun with a Fourne single screw extruder. The take-up speeds were from 2500 to 4500 m/min used. As the spinning speed increased, denier of the filaments decreased from 10 to 4. Figure 4 shows tensile properties of the undrawn PET and PTT filaments at various take-up speeds. PTT fiber spun at 2500 m/min take-up speed shows much lower modulus and tenacity and much higher strain than PET with the same take-up speed. However, PTT and PET fibers spun at 3000 m/min show almost the same modulus and tenacity, but the strain of PPT fiber is still higher than that of PET fiber.

In the case of PEI and PTI, they could not be spun with Fourne single screw extruder. Because these polyesters soften at low temperatures: 110$^\circ$ C for PEI, and 80$^\circ$ C for PTI [3],
the polymer particles stuck together and clung on the walls of the hopper, preventing a proper feeding for these materials. Instead, PEI and PTI were extruded by using Bradford piston type spinning machine. The extrusions were carried out at several different temperatures from 170 to 260° C, but only at 170° C for PTI and 190° C for PEI, can they be continuously extruded. Figure 5 shows the microscopic pictures of the extruded PEI and PTI fibers. Both extruded fibers were very uneven and extremely brittle. PTI fiber shows much smoother surface than PEI fiber. PEI fiber was white and PTI fiber was transparent. Figure 6 shows DSC curves of the PEI fiber. The PEI fiber shows Tg at 60 and 55° C, a tiny exothermic peak (Tcc) at 160 and 180° C, and an endothermic peak at 246 and 242° C in its first and second heating scan, respectively. Also it shows one more very tiny and broad endothermic peak at high temperature (around 295° C) that can be assigned to the cyclic dimer produced as a by-product during the polymerization. The DSC analysis of PTI fiber shows Tg at 43° C in both the first scan and the second scan, but there were no peaks for Tcc and Tm (Figure 7). It has been reported that around 15% of cyclic dimer of ethylene isophthalate was produced during the PEI polymerization [9]. The high melting cyclic dimer might make it hard to spin PEI.
4. CONCLUSIONS

PET, PTT, PEI, and PTI were prepared in 1-gallon Parr reactor by condensation polymerization. The condensation reaction temperatures were 260 ~ 285° C and the pressure varied from 0.4 to 0.6 torr. The polymerization reaction for PEI and PTI occurred much more slowly than for PET and PTT with the same amount of catalysts. The reaction conversions for 1st step (esterification reaction) were almost 100 % for all four polyesters, but in the 2nd step (condensation reaction), the conversions were 78, 88, 70, and 85 % for PET, PTT, PEI, and PTI, respectively. The molecular weights were 28,300, 33,300, and 17,800 g/mole for PET, PTT, and PEI, respectively. The intrinsic viscosity of PTI was 0.54 dL/g. In DSC analysis, PET, PTT, PEI, and PTI show Tg’s at 71, 48, 54, and 43 ° C. PET and PTT show Tcc’s at 144, and 69 ° C, and Tm’s at 253 and 228 ° C, respectively. PEI shows Tg, Tcc, and Tm at 54, 176, and 243 ° C, but the Tcc, Tm peaks’ areas are very tiny, thus confirming that these polymers are predominantly amorphous. PTI does not have either Tcc or Tm. In the case of PEI, it formed different kinds of crystals with different melting points depending on the crystallization methods. The crystals formed by annealing or orientation show the high melting temperature of around 240° C, while the crystals formed from solution by slow evaporation show the low melting temperature of around 124 ° C. All the synthesized polyesters show high thermal stability in TGA analysis. The peak temperatures of the
maximum rate of mass loss were 505, 463, 475 and 426⁰ C for PET, PTT, PEI, and PTI respectively. PET and PTT were melt-spun with Fourne single screw extruder and wound with several take-up speeds from 2500 ~ 4500 m/min. The PTT fiber shows higher strain and lower tenacity than PET fiber. Although, PEI and PTI can be melt-spun using the Bradford piston type spinning machine, the resulting PEI and PTI fibers were very uneven and brittle.
5. REFERENCES


8. Quintana R, Ilarduya AM, Rude E, Kint DPR, Alla A, Galbis JA, Munoz-Guerra S, Poly(ethylene isophthalate)s: effect of the tert-butyl substituent on structure and properties, Polymer,

Table 1. Typical recipes for conventional polymerization

<table>
<thead>
<tr>
<th></th>
<th>PET</th>
<th>PTT</th>
<th>PEI</th>
<th>PTI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Monomer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethyl terephthalate (DMT) (g)</td>
<td>1262</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Terephthalic acid (TPA) (g)</td>
<td>-</td>
<td>1002</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Isophthalic acid (IPA) (g)</td>
<td>-</td>
<td>-</td>
<td>1000</td>
<td>1162</td>
</tr>
<tr>
<td>Ethylene glycol (EG) (mL)</td>
<td>761</td>
<td>-</td>
<td>839</td>
<td>-</td>
</tr>
<tr>
<td>1,3-propanediol (PDO) (mL)</td>
<td>-</td>
<td>1084</td>
<td>-</td>
<td>1265</td>
</tr>
<tr>
<td><strong>Catalyst</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc acetate (Zn-Ac) (g)</td>
<td>0.60</td>
<td>-</td>
<td>0.55</td>
<td>-</td>
</tr>
<tr>
<td>Antimony (III) oxide (Sb-O) (g)</td>
<td>0.50</td>
<td>-</td>
<td>0.90</td>
<td>-</td>
</tr>
<tr>
<td>Titanium butoxide (Ti-B) (g)</td>
<td>-</td>
<td>1.02</td>
<td>-</td>
<td>1.2</td>
</tr>
<tr>
<td><strong>Thermal stabilizer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimethyl phosphate (g)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.58</td>
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<tr>
<td><strong>Stirring speed (RPM)</strong></td>
<td>65</td>
<td>190</td>
<td>65</td>
<td>190</td>
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<tr>
<td><strong>Reaction temp. (°C)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1st step</td>
<td>200</td>
<td>230</td>
<td>200</td>
<td>230</td>
</tr>
<tr>
<td>2nd step</td>
<td>280~285</td>
<td>260~265</td>
<td>260~265</td>
<td>260~265</td>
</tr>
<tr>
<td><strong>Vacuum (torr)</strong></td>
<td>0.4~0.6</td>
<td>0.4~0.6</td>
<td>0.4~0.6</td>
<td>0.4~0.6</td>
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</table>
Table 2. Intrinsic viscosity and molecular weight of conventionally synthesized polyesters

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Commercial PET</th>
<th>Commercial PTT</th>
<th>Polyesters synthesized in Parr reactor</th>
<th>PET</th>
<th>PTT</th>
<th>PEI</th>
<th>PTI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction (polycondensation) conversion (%)</td>
<td>N/A</td>
<td>N/A</td>
<td>78</td>
<td>88</td>
<td>70</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>$V_{\text{int}}$ (dL/g)</td>
<td>0.44</td>
<td>0.88</td>
<td>0.57</td>
<td>0.58</td>
<td>0.45</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>$M_n$ (g/mole)</td>
<td>18,700</td>
<td>64,500</td>
<td>28,300</td>
<td>33,300</td>
<td>17,800</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>
Table 3. DSC data for the PEI

<table>
<thead>
<tr>
<th></th>
<th>PEI synthesized in laboratory scale</th>
<th>Parr-PEI as synthesized</th>
<th>Annealed at 60°C overnight</th>
<th>Melt-cast film</th>
<th>Reprecipitated with chloroform / diethyl ether</th>
<th>Solution-cast with chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tg (°C)</strong></td>
<td>54</td>
<td>58.83</td>
<td>56.02</td>
<td>60.28</td>
<td>56.50</td>
<td>54.46</td>
</tr>
<tr>
<td><strong>Tcc (°C)</strong></td>
<td>N/A</td>
<td>175.54</td>
<td>146.52</td>
<td>149.10</td>
<td>159.12</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Tm (°C)</strong></td>
<td>N/A</td>
<td>242.62 (5.9 J/g)</td>
<td>242.02 (3.7 J/g)</td>
<td>244.37 (4.62 J/g)</td>
<td>242.12 (4.3 J/g)</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Table 4. Thermal degradation temperatures of polyesters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial decomposition temperature (°C)</th>
<th>Onset temperature of decomposition (°C)</th>
<th>$T_{\text{max}}$ a) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial PET</td>
<td>381</td>
<td>448</td>
<td>482</td>
</tr>
<tr>
<td>Commercial PTT</td>
<td>337</td>
<td>426</td>
<td>457</td>
</tr>
<tr>
<td>Parr-PET</td>
<td>413</td>
<td>470</td>
<td>505</td>
</tr>
<tr>
<td>Parr-PTT</td>
<td>345</td>
<td>430</td>
<td>462</td>
</tr>
<tr>
<td>Parr-PEI</td>
<td>350</td>
<td>442</td>
<td>475</td>
</tr>
<tr>
<td>Parr-PTI</td>
<td>340</td>
<td>398</td>
<td>426</td>
</tr>
</tbody>
</table>

$T_{\text{max}}$ is the peak temperature of the maximum rate of mass loss.
Figure 1. Stirring torque change during condensation polymerization
Figure 2. DSC thermograms for conventionally synthesized polyesters in Parr reactor
Figure 3. TGA weight loss curve for commercial and conventionally synthesized polyesters
Figure 4. Tensile property of PET and PTT filaments; ▲: PET, ▣: PTT
Figure 5. Microscopic image of PEI and PTI filaments
Figure 6. DSC curves for PEI fiber; (a) first scan and (b) second scan
Figure 7. DSC curves for PTI fiber (a) first scan and (b) second scan
CHAPTER 3. PREPARATION AND RING-OPENING
POLYMERIZATION OF CYCLIC OLIGOESTERS OF PET, PTT, PEI, AND PTI

1. INTRODUCTION

Usually polymers prepared by condensation polymerization contain cyclic molecules along with linear chains. Conventionally produced polyesters also contain small amounts of cyclic low molecular weight oligomers. Ross et al. [1] and Goodman et al. [2] isolated low molecular weight components from PET film, chip, and fiber by Soxhlet extraction. The total amount of the all extracted compounds was 1.3-1.7 percent by weight. Goodman et al. [2] reported three possible mechanisms for the cyclic compound formation: (1) cyclization of short chain linear oligomers; (2) attack of a polymer hydroxyl end-group on an ester group in its own chain (back-biting); (3) reaction of interchange among ester groups within or between polymer chains. The cyclic oligomers can be prepared deliberately, and used as a feedstock for ring-opening polymerization. The cyclic oligomers can also be obtained by the cyclo-depolymerization (ring-chain equilibrium reaction) of linear polyester polymers [3-6]. This technique is one of the useful methods for recycling of polyesters.

The ring-opening polymerization offers potential advantages relative to the conventional
polymerization process. It does not produce any small molecule by-product and the reaction can be carried out at atmospheric pressure. Also, low melt viscosity of the cyclic oligomers allows processing by various techniques such as pultrusion, resin-transfer molding, melt filtration, or reaction injection molding either concurrent with or just prior to polymerization [7-8]. The cyclic oligoesters, in the molten state, can flow like a thermoset resin, but the finished product retains the properties of the thermoplastic polyester [8].

In this chapter, cyclic oligomers of PET, poly(trimethylene terephthalate) (PTT), poly(trimethylene isophthalate) (PTI), and poly(ethylene isophthalate) (PEI) were prepared by cyclo-depolymerization of the linear polyesters. These cyclic oligoesters were polymerized to a linear polymer with or without a catalyst. The CDP-cyclic oligomers and ROP polyesters were characterized with FTIR, HPLC, and DSC.

2. EXPERIMENTAL

2.1. Materials

Commercial PET and PTT were supplied by DuPont and Shell, respectively. Antimony (III) oxide was supplied by DuPont. Zinc acetate, dibutyltin oxide, trifluoroacetic acid (TFA), chloroform (CLF), phenol, and 1,1,2,2-tetrachloroethane (TCE) were obtained from Aldrich.
2.2. Extraction of commercial polyesters and synthesized polyesters

Cyclic oligoesters were prepared from commercial PET and PTT by Soxhlet extraction of the these polymers with dichloromethane. The extraction time was 24 hrs.

2.3. Preparation of cyclic oligoesters by cyclo-depolymerization (CDP) of polyesters

Commercial PET and commercial PTT were used for CDP. In the case of PEI and PTI, they were synthesized in our lab (see Chapter 3). 10 g of polymer and dibutyltin oxide (3 mol % based on polymer) were dissolved in boiling dichlorobenzene (600 ml). The solution was refluxed for 4 days. The solution was cooled down to room temperature, and some precipitate was obtained, filtered off, and dried. The filtrate was evaporated by using rotary evaporator at 58° C under vacuum and the residue was washed several times with methanol then dried at 60° C under vacuum overnight. The precipitate obtained in CDP of PET and PTT is reported as unreacted polymer [4, 5, 9]. No precipitate was formed in the CDP of PTI. In the case of PEI, the precipitate was reported as a cyclic dimer [3].

2.4. Ring-opening polymerization (ROP) in a polymerization tube

A 0.5 g of cyclic oligomer and of catalyst (0.003 g, 0.5 mol%) were introduced into a flask and mixed by dissolving in dichloromethane. The solvent was slowly evaporated with
vigorous stirring overnight using a magnetic stirrer in order to get homogeneous mixing of ETCs and catalyst. The mixture sample was dried in a vacuum oven at 80° C under vacuum overnight. The mixture was charged into a polymerization tube. The tube was purged with N₂ gas to avoid degradation and then put in a vapor bath charged with boiling triethylene glycol (b. p. of 282° C). The polymerization was occurred at 282° C in a vapor bath under constant nitrogen flow for 1 hour.

2.5. Ring-opening polymerization (ROP) with stirring

A 50 ml polymerization reactor was charged with 5 g of cyclic oligomers and a catalyst (0.5 mol%). The reactor was equipped with a mechanical stirrer and three sidearms. The reaction was carried out under nitrogen flow. The reaction temperature was kept by using a eutectic salt bath mixture of 51.3% potassium nitrate (KNO₃) and 48.7% sodium nitrate (NaNO₃). The reaction was carried out at 260° C for 1 hour with stirring.

2.6. Intrinsic viscosity and molecular weight measurement

Intrinsic viscosity was measured by using an Ubbelohde viscometer in a water bath thermostated at 25° C. The solvent was a mixture of phenol and 1,1,2,2-tetrachoroethane with 60/40 weight ratio. The intrinsic viscosity was estimated from the single-point Billmeyer
method [10] method. The following equation was used:

$$V_{\text{int}} = \frac{1}{4} V_{\text{rel}} + \frac{3 \ln V_{\text{rel}}}{4C},$$

where $V_{\text{int}}$: intrinsic viscosity, $V_{\text{rel}}$: reduced viscosity ($=\frac{(V_{\text{rel}}-1)}{C}$), $V_{\text{rel}}$: relative viscosity ($=\frac{\text{flow time of solution}}{\text{flow time of solvent}}$).

The number-average molecular weights were obtained from the following Mark-Houwink relations [11].

For PET

$$[\eta] = 7.61 \times 10^{-4} M_n^{0.67},$$

for PTT

$$[\eta] = 8.20 \times 10^{-4} M_n^{0.63},$$

and for PEI

$$[\eta] = 8.15 \times 10^{-4} M_n^{0.645}.$$

In the case of PTI, K and $\alpha$ values have not been reported, so its molecular weight could not be measured, and only intrinsic viscosity is reported in this chapter.

2.7. Differential Scanning Calorimetry (DSC) analyses

DSC measurements were conducted on a Perkin-Elmer™ Differential Scanning Calorimeter (DSC-7). During the measurements, N$_2$ gas was purged at a constant flow rate. Indium was
used as a calibration standard. A scanning rate of 20° C/ min was used.

2.8. High-Performance Liquid Chromatography (HPLC) analyses

The measurements were carried out using a Waters 1525 Binary HPLC pump with an Alltech C18 reversed-phase column (250 mm length, 4.6 mm diameter). The mobile phase was acetonitrile (AcN) / trifluoroacetic acid (TFA) gradient with a flow rate of 0.8 ml/min (Table 1). Solvent A was 0.1% TFA aqueous solution and Solvent B was AcN. Samples were prepared by diluting with chloroform or TFA. Detection was provided by a Waters 2487 Dual \( \lambda \) detector set at 254 nm.

2.9. Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectral analyses were carried out in a Nicolet 510P FTIR spectrometer between 4000 and 400 cm\(^{-1}\) with samples in the form of pressed KBr pellets

3. RESULTS AND DISCUSSION

3.1. Preparation and characterization of cyclic oligoesters

The cyclic oligoesters were isolated by extraction from commercial polyesters with boiling dichloromethane in a Soxhlet extraction apparatus for 24 hours. Commercial PET and PTT
included 1.5 and 1.9 % of cyclic oligomer, respectively. Figure 1 shows the HPLC separation of those cyclic oligomers. The HPLC traces show one main peak at retention time of 23.75 and 23.40 minutes for PET and PTT respectively. It implies that size of the extracted cyclic oligomers were very uniform (Figure 1). It is known that cyclic trimer or dimer is usually formed during the polymerization of PET and PTT, respectively.

PET cyclic oligomers (ETCs) and PTT cyclic oligomers (TTCs) were prepared by CDP of commercial PET and PTT, and PEI cyclic oligomers (EICs) and PTI cyclic oligomers (TIC) were prepared by CDP of the PEI and PTI synthesized in a Parr reactor (the procedure is reported in Chapter 3). Table 1 shows molecular weights (or intrinsic viscosity) of those polymers used for the cyclo-depolymerization (CDP). 1,2-dichlorobenzene was used as a solvent for the DCP. Zinc acetate or dibutyltin oxide was used as a catalyst. Unreacted polymer precipitated out in the depolymerization of PET and PTT, and their cyclic oligomer was obtained by evaporation of the filtrate solution in rotary evaporator at 58°C under vacuum. In the case of PEI, the cyclic dimer precipitated out during the reaction. There was nothing precipitated during the depolymerization of PTI. Figure 2 shows HPLC traces for the cyclic oligoesters prepared by cyclo-depolymerization (CDP) of PET with different catalysts. The cyclic oligomers had different sizes, but the main product was trimer having the retention time at 23.75 minutes. The cyclic oligomer compositions depended on the various
catalysts used in cyclo-depolymerization. Figure 3 shows HPLC traces for the cyclic oligoesters prepared by cyclo-depolymerization (CDP) of PTT with different catalysts. Oligomers of several different sizes besides the main product, cyclic dimer (after 23.40 minutes of retention time) were obtained.

Figures 4 and Figure 5 show FTIR spectra for the CDP-ETC and CDP-TTC, respectively. The cyclic oligoesters cannot have trans conformations due to their kinked chemical structure. So the FTIR spectra of cyclic oligomers would show only the bands corresponding to the gauche conformational bands, not the trans conformation bands. Miyake et al [12] investigated the FTIR bands for amorphous PET, crystalline PET, and PET cyclic and linear trimer. The amorphous PET shows gauche configuration bands at 1453, 1370, 1172, 1099, 1042, and 895 cm$^{-1}$ and the crystalline PET shows trans configuration bands at 1471, 988, 972, and 860 cm$^{-1}$[12]. The PET cyclic trimer shows the bands corresponding to the gauche bands, and linear trimer shows both gauche and trans bands. Our CDP-ETC shows the bands at 1453, 1367, 1170, 1096, 1034, and 899 cm$^{-1}$ and they are very similar with the gauche bands (Figure 4) not trans bands. Kim et al. reported the FTIR spectroscopic analysis for amorphous and crystalline PTT [13]. In their paper, the amorphous PTT shows a band at 1577 cm$^{-1}$ and the band disappeared in pure crystalline PTT. A very sharp peak at 938 cm$^{-1}$, which was assigned to the CH$_2$ rocking mode in the crystal, was shown only in the spectrum
of pure crystalline PTT [13]. In the spectrum of CDP-TTC (Figure 5), only the amorphous band at 1580 cm\(^{-1}\) is shown, not the crystalline band at 938 cm\(^{-1}\) (Figure 5). The FTIR results for CDP-ETC and CDP-TTC imply that their structures are of cyclic form.

Figure 6 shows DSC thermograms for the cyclic oligoesters prepared by the CDP of polyesters. PET cyclic oligoesters (CDP-ETC, Figure 6a) show 4 melting peaks at 59, 122, 194, and 276 °C. This implies that the CDP-ETC consists of a distribution of oligomers with several sizes, and they have different melting temperatures. PTT cyclic oligoester (CDP-TTC, Figure 6b) show one melting peak at 241° C. PEI cyclic oligoester (CDP-EIC, Figure 6c) and PTI cyclic oligoester (CDP-TIC, Figure 6d) show a melting peak at 335° C and 147° C, respectively.

3.2. Ring opening polymerization of cyclic oligoesters

Cyclic oligoesters were polymerized in DSC under nitrogen flow without any catalyst for 5 minutes. Around 5 mg of cyclic oligomers were put in DSC aluminum sample pans, and they were heated to the desired temperature, held at that temperature for 5 minutes, and cooled down to 25°C, and then DSC heating curves were recorded from 25°C to desired temperatures at 20°C per minute. Figure 7 shows such DSC curves. The CDP-ETC was heated to 330° C and kept at this temperature for five minutes, after that, the melting peak at
317°C disappeared and Tg, Tcc, and Tm were shown at 73, 159, and 238°C (Figure 7a). The cyclics were converted into linear polymer even without catalyst. The CDP-TTC shows still the melting temperature at 242°C (Figure 7b) after holding at 260°C for five minutes. The PTT cyclic oligomers are more stable than CDP-ETC. The CDP-EIC were heat-treated at 340°C for 5 minutes, and after that, Tg could be observed at 57°C, but a high Tm was still observed at 320°C (Figure 7c). Thus, the polymerization occurred partially. The melting peak of CDP-TIC was no longer shown at 146°C after the heat-treatment in the DSC instrument at 260°C for 5 minutes, and there were not any Tcc and Tm peaks seen, like for the conventionally synthesized PTI (see Figure 7d). The PTI cyclic oligomer also could be polymerized at 260°C without catalyst. TTC and EIC might be more stable than ETC and TIC.

The cyclic oligomers were also polymerized with antimony(III) oxide as a catalyst. Figure 8 and Figure 9 show the DSC curves for the ROP-PET and ROP-PTT samples obtained from ring-opening polymerization of CDP-ETC and CDP-TTC in the presence of 0.5 mol% of antimony (III) oxide as a catalyst. The polymerization was carried out at 282°C, in the polymerization tube, under nitrogen flow, for one hour. ROP-PET shows Tg, Tcc, and Tm at 70, 132, and 248°C, and all peaks for CDP-ETC melting at 59, 122, 194, and 276°C
disappeared. The number average molecular weight obtained from solution viscosity was 3,000 g/mol. ROP-PTT shows Tg, Tcc, and Tm at 47, 75, and 222°C, and the melting peak of CDP-TTC at 241°C disappeared. The number average molecular weight obtained from solution viscosity was 8,800 g/mol. ROP-PEI was also prepared by ROP of CDP-EIC at 260°C for 1 hour. The CDP-EIC was melted at 340°C for 1 minute and cooled down to the polymerization temperature, 260°C within 5 minutes with stirring to mix with catalyst.

Figure 10 shows the DSC curve for the ROP-PEI. It shows a glass transition at around 73°C, which is much higher than that of conventionally synthesized PEI (see Chapter 3), but the glass transition temperature went down to 62°C in the second heating scan. Also a very broad and small crystallization peak and a melting peak are shown at around 149 and 246°C, while the sharp melting peak for CDP-EIC at 335°C disappeared. The number average molecular weight of the ROP-PEI was 7,200 g/mol. Figure 11 shows DSC curve for the ROP-PTI prepared by ROP of CDP-TIC at 260°C for 1 hour. It shows a glass transition at around 40°C, and melting peak of CDP-TIC at 147°C disappeared. The intrinsic viscosity of the ROP-PTI was 0.25 dL/g.
4. CONCLUSIONS

Cyclic oligomers of PET, PTT, PEI, and PTI were synthesized by cyclo-depolymerization of the linear polyester; PET, PTT, PEI, and PTI, using 1,2-dichlorobenzene as a solvent in the presence of zinc acetate or dibutyltin oxide. The CDP-ETC and CDP-TTC were mixtures of several sized oligomers including mainly trimer and dimer. In FTIR spectra, the ETC and TTC did not show any crystalline bands, but only amorphous bands, which implies their structures were the cyclic forms. The melting temperatures were 59, 122, 194, and 276 °C for CDP-ETC, 241° C for CDP-TTC, 335° C for CDP-EIC, and 147° C for CDP-TIC. In the second scan of DSC after a 5-minute hold at high temperature, the melting peaks shown in the first DSC scan of CDP-ETC, CDP-TIC, and CDP-EIC disappeared and new peaks for Tg, Tcc, and Tm were observed. In the case of CDP-TTC, there was no change between the first and the second scan. This implies CDP-ETC, CDP-TIC, and CDP-EIC could be polymerized without catalyst in 5 minutes in DSC, but CDP-TTC could not be converted into the polymer.

The cyclic oligoesters were also polymerized in the polymerization tube with antimony(III) oxide as a catalyst. The molecular weights of ROP polymers were 3,000 g/mol of PET, 4,900 g/mol for PTT, and 7,000 g/mol for PEI. The intrinsic viscosity of ROP-PTI was 0.25 dL/g. The ROP polyesters show very similar thermal properties with regular polyesters in their DSC analyses, even though their molecular weights were not as high.
5. REFERENCES


2. Goodman I and Nesbitt BF, The structures and reversible polymerization of cyclic oligomers from poly(ethylene terephthalate), Polymer, 1, 384 (1960)


8. Tullo A, Best of both worlds, Cyclic Corp. Hopes that a new twist on polybutylene terephthalate will create a niche, C&EN, 4, 22 (2002)


Table 1. HPLC Gradient

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Flow rate (ml/min)</th>
<th>Solvent A (%)</th>
<th>Solvent B (%)</th>
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</thead>
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<tr>
<td>0</td>
<td>0.8</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>10</td>
<td>0.8</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>20</td>
<td>0.8</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>33</td>
<td>0.8</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>35</td>
<td>0.8</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>35.01</td>
<td>0.8</td>
<td>90</td>
<td>10</td>
</tr>
</tbody>
</table>
Table 2. Intrinsic viscosity and molecular weight of polyesters used for the cyclo-depolymerization

<table>
<thead>
<tr>
<th></th>
<th>PET</th>
<th>PTT</th>
<th>PEI</th>
<th>PTI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{\text{int}}$ (dL/g)</td>
<td>0.44</td>
<td>0.88</td>
<td>0.45</td>
<td>0.54</td>
</tr>
<tr>
<td>$M_n$ (g/mole)</td>
<td>18,700</td>
<td>64,500</td>
<td>17,800</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure 1. HPLC traces for cyclic oligomers extracted from commercial PET and PTT
Figure 2. HPLC chromatograms of cyclic oligoesters obtained by CDP of PET with (a) dibutyltin oxide and (b) zinc acetate as a catalyst for 2 days.
Figure 3. HPLC chromatograms of cyclic oligoesters obtained by CDP of PTT with (a) dibutyltin oxide and (b) zinc acetate as a catalyst for 2 days.
Figure 4. FTIR spectrum for CDP-ETC
Figure 5. FTIR spectrum for CDP-TTC
Figure 6. DSC thermograms for CDP cyclic oligoesters for (a) PET, (b) PTT, (c) PEI, and (d) PTI
Figure 7. DSC curves for (a) PET, (b) PTT, (c) PEI, and (d) PTI obtained from polymerization of CDP cyclic oligoesters in DSC without catalyst.
Figure 8. DSC thermogram of ROP-PET obtained by ring-opening polymerization of CDP-ETC; with 0.5 mol% of antimony(III) oxide at 282° C for 1 hour
Figure 9. DSC thermogram of ROP-PTT obtained by ring-opening polymerization of CDP-TTC; with 0.5 mol% of antimony(III) oxide at 282° C for 1 hour
Figure 10. DSC thermogram of ROP-PEI obtained by ring-opening polymerization of CDP-EIC; with 0.5 mol% of antimony(III) oxide at 260º C for 1 hour
Figure 11. DSC thermogram of ROP-PTI obtained by ring-opening polymerization of CDP-TIC; with 0.5 mol% of antimony(III) oxide at 260° C for 1 hour
CHAPTER 4. RING-OPENING POLYMERIZATION OF

POLY(TRIMETHYLENE TEREPTHALATE) CYCLIC DIMER

1. INTRODUCTION

Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) have been produced commercially for more than 50 years. Poly(trimethylene terephthalate) (PTT) was commercialized very recently. A number of studies on PTT polymer have been reported [1-4, 8]. The commercial polyesters have been manufactured by condensation polymerization. Usually, polymers prepared by the condensation polymerization contain cyclic molecules along with the linear chains, and conventionally produced polyesters also contain small amounts of cyclic low molecular weight oligomers. The cyclic oligomers create some problems during polyester processing, but also they can be used as a feedstock for ring-opening polymerization. Recently research on the conversion of cyclic oligoester into linear polymer has received some attention [5, 6, 9]. The low melt viscosity of the cyclic oligomers allows processing by various techniques such as pultrusion, resin-transfer molding, melt filtration, or reaction injection molding either concurrent with or just prior to polymerization [5, 6]. Cyclics Corporation produces the cyclic oligomers of butylene terephthalate (CBT), as a mixture of dimer, trimer, and tetramer. These oligomers are made by breaking down
poly(butylene terephthalate) (PBT) [6]. CBT can be polymerized back into PBT in the presence of a transesterification catalyst. CBT, in the molten state, can flow like a thermoset resin into the glass or carbon fiber reinforcing material in composites, but the finished product retains the properties of the thermoplastic PBT [6]. Hodge et al. [9] and Wan et al. [10] reported the preparation of PTT cyclic dimer by cyclo-depolymerization of PTT or by reaction of 1,3-propanediol with terephthaloyl chloride under dilute conditions and the ring-opening polymerization. Hodge et al. polymerized the dimer, but it was done in vacuum oven at 300° C and the molecular weight was 30,300 g/mol [9]. Wan el al. polymerized the dimer at 250° C for 15 minutes with several catalysts and the inherent viscosity was 0.49 dL/g when antimony(III) oxide was used as a catalyst [10]. However, systematic research has not been reported on the ring-opening polymerization of PTT cyclic dimer with various catalysts by using a real polymerization reactor.

In this chapter, the ring-opening polymerization of PTT cyclic dimer is investigated with several catalysts. The effect of catalyst concentration is determined on the number average degree of polymerization. Thermal properties of PTT polymers are also presented.
2. EXPERIMENTAL

2.1. Materials

Crude PTT cyclic dimer and antimony(III) oxide were obtained from a conventional PTT manufacturing plant (DuPont in Kinston, NC). Dibutyltin oxide, titanium butoxide, and titanium isopropoxide were obtained from Aldrich. Phenol, dichloromethane and 1,1,2,2-tetrachloroethane (TCE) were obtained from Aldrich.

2.2. Purification of PTT cyclic dimer

The crude dimer was washed with water and ethanol several times and dried in vacuum oven overnight in order to remove any remaining traces of 1,3-propanediol. Then, the washed dimer was dissolved in dichloromethane. When the solution became completely clear, the contaminants, namely polymer particles were filtered off. The solution was kept agitated by stirring for 24 hours with silica gel to remove any other polar impurities. The silica gel was filtered off again, and the solvent was evaporated by using a rotary evaporator. Finally the purified dimer was washed with acetone several times and dried in vacuum oven overnight.
2.3. Ring-opening polymerization (ROP) of PTT cyclic dimer

A 50ml polymerization reactor was charged with 5 grams cyclic dimer and catalysts with various concentrations. The reactor was equipped with a mechanical stirrer and three sidearms. The reaction was carried out under a nitrogen flow. The reaction temperature was kept by using an eutectic salt bath mixture of 51.3% potassium nitrate (KNO₃) and 48.7% sodium nitrate (NaNO₃). The reaction was carried out at 260° C for 1 hour with stirring. Antimony(III) oxide (Sb-O), dibutyltin oxide (DBO), titanium(IV) butoxide (Ti-B), and titanium(IV) isopropoxide (Ti-I) were used as catalysts. In the case of Ti-I, 100ppm was used for the reaction, and it was injected with a syringe, using a catalyst solution in diphenyl ether. 0.1mL of the catalyst solution was injected after the dimer was melted completely. The catalyst solution was made by dissolving 0.05438 g of Ti-I in 10mL phenyl ether (0.5438 % w/v). The ROP polymers were purified with Soxhlet extraction with dichloromethane overnight.

2.4. Intrinsic viscosity and molecular weight measurement

Intrinsic viscosity was measured by using an Ubbelohde viscometer in a water bath thermostated at 25° C. The solvent was a mixture of phenol and 1,1,2,2-tetrachoroethane with 60/40 weight ratio. The intrinsic viscosity was estimated from the single-point Billmeyer
method [7]. The following equation was used:

\[ V_{\text{int}} = \frac{1}{4} V_{\text{red}} + \frac{3\ln V_{\text{rel}}}{4C} \]

where \( V_{\text{int}} \): intrinsic viscosity, \( V_{\text{red}} \): reduced viscosity \( (\frac{(V_{\text{rel}} - 1)}{C}) \), \( V_{\text{rel}} \): relative viscosity \( (= \text{flow time of solution/flow time of solvent}) \).

The number-average molecular weights were obtained from the following Mark-Houwink relations [8].

\[ [\eta] = 8.20 \times 10^{-4} M_n^{0.63} \]

2.5. Differential Scanning Calorimetry (DSC) analyses

DSC measurements were conducted on a Perkin-Elmer™ Differential Scanning Calorimeter (DSC-7). During the measurements, \( N_2 \) gas was purged at a constant flow rate. Indium was used as a calibration standard. The scanning rates of 20° C/ min were used.

3. RESULTS AND DISCUSSION

The crude dimer was collected as a byproduct during the conventional polymerization process in the PTT plant. The as-received dimer was in 1,3-propanediol and could not be used for polymerization. It had to be washed with water and ethanol and dried under vacuum to remove 1,3-propanediol. The washed dimer had some small amount of polar impurities
(mostly linear oligomers) as observed in thin layer chromatography (TLC) analysis. The 
impurity can be removed by stirring the dimer in dichloromethane with silica gel. Figure 1 shows DSC thermogram of the purified cyclic dimer. It shows a sharp melting peak at 254°C. The purified dimer was polymerized with several different catalysts at different concentrations. The reaction occurred in a 50ml reaction flask equipped with 4 armed flask head for mechanical stirrer and nitrogen gas in and out, at 260°C for 1 hour. Antimony(III) oxide, dibutyltin oxide, titanium(IV) butoxide, and titanium(IV) isopropoxide were used as catalysts. The obtained polymer samples were purified with methylene chloride in Soxhlet extraction apparatus for 24 hours in order to remove unreacted dimer. Figure 2 shows the DSC curves of PTT obtained by ring-opening polymerization of the cyclic dimer with different catalysts. Table 1 shows the melting temperatures from the DSC data. After the polymerization with a catalyst, the melting peak of cyclic dimer at 254°C disappeared. The melting peak for PTT polymers were observed at around 230°C, and the heats of fusion were around 60~70 J/g. This is similar with the melting peak of regular commercial PTT, around 228°C. In the case of the sample prepared without catalyst, its DSC curve still shows a melting peak at 254°C, even though it has also a tiny broad endothermic peak at around 203°C. Also the PTT polymerized without catalyst shows only 5 % conversion (Table 2). The two peaks at 203 and 254°C might be from the 5% of polymer and 95% of the unreacted
cyclic dimer, respectively. The molecular weight of the polymer without catalyst was 6,155 g/mol (Table 2). The other polymers prepared with catalysts have number-average molecular weights (Mn), 18500~27000 g/mol (Table 2). Among the catalysts, titanium(IV) butoxide gives the highest number average molecular weight of 27,200 g/mol and 95% conversion. This catalyst is the more effective than other catalysts to obtain high molecular weight and high conversion.

The cyclic dimer was also polymerized with several concentrations of antimony(III) oxide and titanium(IV) butoxide. Figure 3 and figure 4 show the DSC curves for the PTT polymers obtained with different concentration of antimony(III) oxide and titanium butoxide respectively. The polymer prepared with 0.25 mol% (Figure 3a) of antimony catalyst shows two melting peaks at 220 for polymer and 252°C for unreacted dimer. After Soxhlet extraction with dichloromethane, the peak at 252°C disappeared. The other polymers prepared with concentrations of 0.5 and 1 mol% (Figure 3b and 3c) show melting peaks at around 228°C. All of the polymers prepared with titanium (IV) butoxide catalyst show a melting peak at around 228°C for all the catalyst concentrations (Figure 4).

Figure 5 shows Mn and conversion changes as a function of the concentration of antimony(III) oxide. The molecular weight and conversion increased with increasing concentration of the catalyst. The highest molecular weight and reaction conversion (31,551
g/mol and 82 %) were obtained when 1 mol% of antimony(III) oxide was used. Figure 6 shows Mn and reaction conversion change as the concentration of titanium (IV) butoxide. The Mn was highest at 0.25 mol% concentration (40,000 g/mol with 77 % conversion) and decreased at higher concentrations. The highest conversion of 95% (Mn of 27,000 g/mol) was accomplished at 0.5 mol% antimony(III) oxide.

4. CONCLUSIONS

PTT can be prepared by ring-opening polymerization of its cyclic dimer collected as a byproduct in the manufacturing process. The PTT cyclic dimer formed during the manufacturing has usually been collected and thrown away. We report that this cyclic oligomer can be converted to the linear polymer by the ring opening polymerization with various catalysts. The polymerization was carried out in a round bottom polymerization reactor at 260°C for 1 hour. Antimony(III) oxide, titanium(IV) butoxide, dibutyltin oxide, and titanium(IV) isopropoxide were used as catalysts. The unreacted cyclic dimer was extracted by Soxhlet extraction. The PTTs obtained by the ring-opening polymerization show very similar DSC curves with that of conventionally synthesized PTT, implying that the cyclic dimer was converted to the linear PTT polymer. The highest molecular weight was 40,000 when 0.25 mol% of titanium(IV) butoxide was used as a catalyst. The PTTs obtained
from the polymerization catalyzed by increasing amounts of antimony(III) oxide have higher molecular weights and reaction conversions. When 1mol% of antimony(III) oxide was used, the molecular weight was 32,000 g/mol and the conversion was 82 %. In the case of polymer catalyzed by titanium (IV) butoxide, the molecular weight and the conversion were 40,000 g/mol and 77 % when 0.25 mol% was used, while 0.5 mol% catalyst produced a molecular weight of 27,000 g/mol and the conversion was 95 %.

5. REFERENCES


6. Tullo A, Best of both worlds, Cyclic Corp. Hopes that a new twist on polybutylene terephthalate will create a niche, C&EN, 4, 22 (2002)


Table 1. Melting temperatures and heat of fusions of the ROP polymers in DSC analyses

<table>
<thead>
<tr>
<th></th>
<th>ROP-PTT-Sb(^{a)})</th>
<th>ROP-PTT-Sn(^{b)})</th>
<th>ROP-PTT-ti-B(^{c)})</th>
<th>ROP-PTT-ti-I(^{d)})</th>
<th>Regular PTT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Temperature (° C)</td>
<td>233</td>
<td>230</td>
<td>232</td>
<td>230</td>
<td>228 (vb)</td>
</tr>
<tr>
<td>Heat of fusion (J/g)</td>
<td>57</td>
<td>65</td>
<td>69</td>
<td>58</td>
<td>81</td>
</tr>
</tbody>
</table>

\(^{a)}\) ROP-PTT-Sb: ring-opening polymerized PTT with antimony(III) oxide 0.5 mol%

\(^{b)}\) ROP-PTT-Sn: ring-opening polymerized PTT with dibutyltin(III) oxide 0.5 mol%

\(^{c)}\) ROP-PTT-ti-B: ring-opening polymerized PTT with titanium(IV) butoxide 0.5 mol%

\(^{d)}\) ROP-PTT-ti-I: ring-opening polymerized PTT with titanium(IV) isopropoxide 0.15 mol%

vb = very broad peak
<table>
<thead>
<tr>
<th></th>
<th>ROP-PTT-no catalyst</th>
<th>ROP-PTT-Sb</th>
<th>ROP-PTT-Sn</th>
<th>ROP-PTT-ti-B</th>
<th>ROP-PTT-ti-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic viscosity (dL/g)</td>
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<td>0.49</td>
<td>0.40</td>
<td>0.51</td>
<td>0.50</td>
</tr>
<tr>
<td>Mn (g/mol)</td>
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<td>26,000</td>
<td>18,500</td>
<td>27,200</td>
<td>26,400</td>
</tr>
<tr>
<td>Extracted cyclics (%)</td>
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<td>6</td>
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<tr>
<td>Conversion (%)</td>
<td>5</td>
<td>79</td>
<td>94</td>
<td>95</td>
<td>49</td>
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Figure 1. DSC thermogram of PTT cyclic dimer
Figure 2. DSC thermograms for ROP-PTT obtained by ring-opening polymerization with (a) no catalyst, (b) antimony(III) oxide, (c) titanium(IV) butoxide, (d) dibutyltin oxide, and (e) titanium(IV) isopropoxide.
Figure 3. DSC thermograms for PTT polymers obtained by ring-opening polymerization of Dupont TTC dimer with (a) 0.25, (b) 0.5, and (c) 1 mol% of antimony(III) oxide (before extraction with methylene chloride)
Figure 4. DSC thermograms for PTT polymers obtained by ring-opening polymerization of Dupont TTC dimer with (a) 0.25, (b) 0.5, and (c) 1 mol% of titanium(IV) butoxide
Figure 5. Graph of (a) number average molecular weight ($M_n$) of ROP-PTT and (b) reaction conversion versus concentration of Sb$_2$O$_3$ used for the polymerization.
Figure 6. Graph of (a) number average molecular weight (Mn) and (b) reaction conversion versus concentration of titanium(IV) butoxide used for the polymerization.
CHAPTER 5. GAS BARRIER CHARACTERIZATION OF

POLY(ETHYLENE TEREPTHALATE) AND POLY(ETHYLENE ISOPHTHALATE)

PEI was synthesized for this research using essentially a condensation polymerization of isophthalic acid and ethylene glycol catalyzed by zinc acetate and antimony trioxide. Several samples were obtained, and their characteristics were observed and compared with PET. The synthesized PEI samples were chemically identified by $^1$H NMR. Thermal analysis (DSC) yielded results that indicate that the samples were primarily amorphous, with a glass transition temperature of 65 – 67° C. Molecular weights of these PEI samples were also obtained, through intrinsic viscosity measurements (Mark-Houwink equation). Molecular weights varied with conditions of the polymerization, and the highest molecular weight achieved was 21,000 g/mol. Finally, the diffusion coefficient, solubility, and permeability of CO$_2$ gas in PEI were measured and found to be substantially lower than in PET, as anticipated from their isomeric chemical structures. This is because in PET the phenyl rings are substituted in the para (1,4) positions, which allows for their facile flipping, effectively permitting gases to pass through. However, the meta-substituted phenyl rings in PEI do not permit such ring flipping, and thus PEI may be more suitable for barrier applications.
1. INTRODUCTION

Poly(ethylene isophthalate) (PEI) is a relatively unexplored polyester, although its structural isomer, poly(ethylene terephthalate) (PET), has been researched, developed, and used for decades. PEI, like its structural isomer PET, is a long, high molecular weight polyester chain, with a repeat unit \((\text{C}_{10}\text{H}_{8}\text{O}_{4})\) containing backbone phenyl rings with carboxyl groups attached in the meta positions (1,3). PEI has not been used in industry, although the conformational characteristics of its phenyl rings [1] would suggest potential uses in applications where PET would not suffice. Although PET is widely used because of its good thermal and chemical resistance and mechanical properties, many studies of blends or copolymers of PET with other polyesters have been reported [5-9]. Copolymers of PET are of significant commercial interest, since the insertion of certain other ester repeat units, such as ethylene 2,6-naphthalate, into PET improves its gas barrier properties. Loss of \(\text{CO}_2\) from carbonated beverage packages and ingress of atmospheric \(\text{O}_2\) into packages containing oxygen-sensitive products can limit shelf life, so improved gas barrier properties can increase package performance.

PEI has almost the same chemical structure as PET except its carbonyl groups are attached in the 1,3-meta positions of its phenyl rings instead of the 1,4-para positions. Figure 1 shows the structures of PEI and PET. The parallel, colinear attachment of ethylene glycol diester to the
phenyl rings in PET allows for flipping of the rings [1]. However, due to the non-colinear attachment of the phenyl rings in PEI, the phenyl rings of PEI may not be flipped. The flipping of phenyl rings may allow gases to permeate through, using the flipping phenyl rings much like a trap door or valve. Thus, if PEI has a lower gas permeability, it can possibly be substituted for PET in applications where this is an important consideration, without sacrificing the other benefits of PET. In this paper we designed an experimental set-up to determine the reaction conditions required for the polymerization of high molecular weight PEI. Also the sorption and diffusion properties of CO₂ gas in PEI were measured and compared with those in PET, and CO₂ permeabilities in both PEI and PET were determined.

2. EXPERIMENTS

2.1. Polymer synthesis

2.1.1 Preparation of bis-(2-hydroxyethyl) isophthalate (BHEI) monomer

The BHEI monomer was synthesized from isophthalic acid (IPA) (powder, 99%) and ethylene glycol (EG) (liquid), according to the reaction in Figure 2. Ethylene glycol (Du Pont) was a fiber-grade reagent, and isophthalic acid (Aldrich) was of 99% purity. The reaction was carried out under a constant flow of nitrogen, in a four-necked autoclave, equipped with a stirrer, thermometer, N₂ input, and condenser/N₂ output. The reactor was
heated with an electric heating mantle, and the heating rate controlled by a Variac. In a
typical run, the autoclave was charged with EG and IPA in a molar ratio of 2.5:1. A slight
excess of EG was used, as it also served as the solvent for the reaction product. Two catalysts
were also added to the reaction mixture: zinc acetate (Zn(CH₃COO)₂) (0.2145g, 0.15% based
on weight of IPA), and antimony trioxide (Sb₂O₃) (0.0715g, 0.05% based on weight of IPA).
The reaction was carried out at the reflux temperature of EG (197º C). At the beginning of the
reaction, IPA remained unchanged and undissolved in EG. However, as the reaction
progressed, IPA slowly reacted with EG. The reaction was completed after 5hrs, whereupon a
clear solution was formed. In order to prevent the oxidation of BHEI monomer, the nitrogen
flow was maintained during the cooling of the autoclave. After cooling to ambient
temperature (~25ºC), the monomer partially solidified into an extremely viscous, white
material.

2.1.2. Synthesis of Polymers

The polymerization occurred in a specialized reaction tube, which consisted of a long,
straight tube with a neck and downward sidearm. The top neck of the tube was used for N₂
input and/or vacuum application. The N₂/vacuum switch consisted of a manifold above the
tube with dual-valve stopcocks. The sidearm was connected to a small round bottom flask,
which was used for collection of distilled ethylene glycol, and a N₂/vacuum output. This thin tube held the previously synthesized monomer, while it underwent polymerization, in the vapor bath of a boiling liquid. Ethylene glycol, methyl salicylate, diphenylmethane, and tri(ethylene glycol) were used as the liquids for the corresponding temperature. The vapor bath was contained in a larger tube with an upward sidearm and the smaller tube was held just above the boiling liquid’s surface (where the temperature is the most constant). The liquid used to create this constant-temperature bath was different for each sample, as modifications were made in each successive trial. The larger tube was heated by a Precision™ heater, and contained boiling stones to prevent violent boiling. Approximately 5-10 g of the BHEI was placed into the polymerization tube. The tube was connected to the N₂/vacuum manifold, and all parts sealed with high-vacuum grease. The tube was then purged of all air, the pressure reduced to around 1 mmHg, and then refilled with nitrogen. This switching process was repeated 2-3 times, and finally ended with the tube under a steady N₂ flow. The tube was then placed into the first vapor bath, boiling methyl salicylate (boiling point of 222° C) or ethylene glycol (b. p. of 197° C). The tube was heated until the monomer melted for 1.5-5.25 hours. At this point, the tube was quickly transferred to the next bath, boiling tri(ethylene glycol) (b. p. of 285° C) or diphenylmethane (b. p. of 264° C). The tube was heated for 1.5-3.5 hours, after which ethylene glycol was slowly removed.
While still in the second vapor bath, the pressure was slowly lowered to purge the tube of N₂. This was done very slowly, as the melt was very sensitive to pressure changes, and would splatter inside the tube if the pressure was lowered too rapidly. Finally, after the pressure was reduced to 1.5-0.55 mmHg, the samples were heated for an additional 1.5-3.5 hours under vacuum, at 285 or 264° C. The detailed reaction conditions for each sample are listed in Table 1, and the reaction mechanism is shown in Figure 3.

**2.2. Molecular Weight Determination from Intrinsic Viscosities**

All intrinsic viscosities (IV) were measured at 25° C in an Ubbelohde viscometer. The mixture of phenol and 1,1,2,2-tetrachloroethane (TCE) (60/40, w/w) was used as the IV solvent. The viscosity-average molecular weights were obtained from the following Mark-Houwink relations [2].

For PET

\[ [\eta] = 7.61 \times 10^{-4} M_n^{0.67} \]

and for PEI

\[ [\eta] = 8.15 \times 10^{-4} M_n^{0.645} \]
2.3. DSC measurements

DSC measurements were conducted on a Perkin-Elmer™ Differential Scanning Calorimeter (DSC-7). During the measurements, N₂ gas was purged at a constant flow rate. The specimens were heated from 25 to 280° C at 10° C/min. and indium was used as a calibration standard.

2.4. NMR measurements

Samples were dissolved in a mixture of trifluoroacetic acid (TFA) and deuterated chloroform (CDCl₃) (1/3, v/v). ¹H NMR spectra were obtained with a 500 MHz Bruker DRX NMR spectrometer. TMS (tetramethylsilane) was used as the internal standard.

2.5. Gas Barrier Characterization

2.5.1. Film preparation

Films for sorption tests were prepared by a melt-press method using a hot-plate press. The polymer was melted between the hot plates and then pressed at 150 and 270° C for PEI and PET respectively. The films were quenched by quickly transferring from the hot press to cold ice water to avoid, as much as possible, crystallization. The film thickness, which is an
average of values from the measurements at 10-15 different points of the films using a micrometer, was around 0.07 mm.

2.5.2. Density

Densities of the polymer films prepared from the melt-press method were measured by using a density gradient technique at 25°C. Toluene (0.865g/cm³) and carbon tetrachloride (1.594g/cm³) were used for the density gradient column.

2.5.3. Wide-Angle X-ray Diffraction (WAXD)

WAXD measurement was carried out with a Siemens type-F X-ray diffractometer. Ni-filtered Cu Kα radiation source with a wavelength of 1.54Å was used in the measurement. The supplied voltage and current were 30 kV and 20 mA, respectively. The amorphous film sample was scanned from 2θ = 5 to 30 - 35°.

2.5.4. CO₂ Gas Sorption Test

An electrobalance (Cahn) was used and set in a sealed glass chamber. 0.5 ~ 0.8 g of a film sample was then placed on one end of the electrobalance, and the same weight as the sample was placed on the other end. The film sample was initially degassed to remove air by applying vacuum in the chamber. Then CO₂ gas was introduced into the sample chamber at a pressure about 460–490 torr. The weight gains were continuously monitored electronically with the electrobalance continuously at 30°C until no more weight gain was shown.
3. RESULTS AND DISCUSSION

3.1. Polymer Synthesis and Molecular Weights

The samples of PEI prepared under different reaction conditions had different molecular weights (Table 1). Sample 5 was created under a noticeably long first heating time of 5.25 hours. This led to the adequate removal of ethylene glycol, but as the second and third heating steps were short (2 and 1.5 hours, respectively), the polymer had a low molecular weight, and was brittle. Samples 3 and 4 were obtained under lower temperatures (222 and 264° C) in the second and third steps, and they have lower molecular weights than sample 5. Sample 6 was nearly opposite in characteristics, as it was very hard, but amber in color. The conditions for sample 6 were different as well, as the first heating was very short (1.5 hr), the second heating the same, and the third heating three times as long as that of sample 5. Thus, sample 6 was heated under vacuum for a much longer time, and had more time to polymerize. Thus, higher reaction temperature produced higher molecular weight PEI. Also, at the same temperature, the molecular weights increase with longer reaction times. However, the color of sample 6 was yellow rather than clear white. That means some thermal degradation occurred during the reaction due to the high reaction temperature. In the case of sample 7, which has the highest molecular weight, the reaction was carried out at somewhat lower temperature (264° C) than samples 5 and 6. Also the reaction time was not as long. Instead,
the vacuum level in the third step was very low. The color of sample 7 was clear white. Therefore, if a high vacuum system is used for the polymerization step, high molecular weight can be obtained even at lower temperatures and for shorter reaction times. Samples 6, 7, and 8, which have relatively high molecular weights, could be made into films, but the others could not, because the low molecular weight polymers likely were not sufficiently entangled to form tough films. Instead, these films were brittle. This implies that PEI should have a molecular weight of at least 17,000 g/mol in order to be a film-forming material.

3.2. Identification and Thermal Behavior

Figure 4 is a typical $^1$H NMR spectrum for the samples produced in our laboratory, and shows the resonance peaks expected for PEI. All samples exhibited nearly identical spectra, with three aromatic proton peaks representing the different protons around the phenyl ring. The peak at 8.7 ppm belongs to the 2-protons (a) on the phenyl ring, the largest peak at 8.25 ppm belongs to the 4,6-protons (b) on the phenyl ring, and the peak at 7.6 ppm corresponds to the 5-protons on the ring (c). The peak at 4.8 ppm is from the methylene groups in the PEI chain (d).

DSC thermograms for a commercial PET and our PEI sample 7 are shown in Figure 5. The first critical points of the curves for PET and PEI were at 71 and 58°C respectively, which
indicated their glass transition ($T_g$) temperatures. Also, PET shows a crystallization peak at 144° C and a melting peak at 253° C. However, PEI does not have any other transition peaks except the glass transition temperature. This implies that PEI is difficult to crystallize and remains largely amorphous. Actually, it has been reported that PEI shows no crystallinity, and some attempts were made to find the proper treatments to induce it to crystallize. [3-4]

3.3. Gas Barrier Characterization

Almost completely amorphous films were prepared for the gas sorption tests, because gas permeability properties are affected by crystallinity. Usually amorphous samples have higher permeabilities than crystalline samples [9, 10]. Figure 6 shows the wide-angle x-ray diffraction pattern for the PEI film used in the gas sorption test. The PEI film was amorphous, as seen in its X-ray pattern, which does not show any crystalline diffraction peaks.

Diffusion coefficients of gases in polymers are conveniently measured using gravimetric methods that utilize an electrobalance apparatus. The weight gain of the sample is measured versus time in an atmosphere of pure penetrant maintained at constant temperature and pressure for several days. The sorption data were collected with a computer linked directly to the electrobalance, and they were plotted against the square root of time. Figures 7 and 8
present the CO₂ sorption curves for the PET and PEI samples, respectively. Diffusion coefficients (D) and infinite values of penetrant mass (M₂) were determined from the hybrid-one term curve fit of the data. The curve fittings were carried out by using Kaleidagraph 3.0 software, which employs the Marquardt nonlinear regression algorithm. The hybrid-one term curve fit is defined below [11].

\[ \frac{M_t}{M_\infty} = \phi(x)f(x) + [1 - \phi(x)]g(x) \]

where \( x = Dt/h^2 \), \( f(x) = 4(x/\pi)^{0.5} \), \( g(x) = 1 - (8/\pi^2)e^{-\pi^2x} \), and \( \phi(x) \) is the weighting function. D and M₂ values from the above curve fits are listed in Table 2. As expected from its chemical structure [1], PEI shows lower D and M₂ values than PET.

Solubility coefficients \( S \) and permeabilities \( P \) can also be calculated from D and M₂ values using the following equations [6].

\[ S = M_\infty \times \frac{\rho}{MW_{penetrant}} \times \frac{22414}{p} \]

\[ P = DS \]

where \( D \) is diffusion coefficient \( (cm^2/s) \), \( P \) is permeability \( (cm^3/cm \cdot s \cdot Pa) \), \( S \) is solubility coefficient \( (cm^3(STP)/cm^3 \cdot Pa) \), \( M_\infty \) is penetrant mass uptake at \( t=\infty \) \( (mg/g \ of \ polymer) \), \( \rho \) is density of sample \( (g/cm^3) \), \( MW_{penetrant} \) is the molecular weight of penetrant \( (g/mol) \), \( p \) is pressure \( (Pa) \), and 22414 is a conversion factor \( (cm^3/mol \ (STP)) \). The densities \( (\rho) \) were
measured by using the density gradient method, and crystallinities \((X_c)\) for the films used for the gas sorption test were calculated from the following equation

\[
X_c = \frac{\rho - \rho_a}{\rho_c - \rho_a}
\]

where \(\rho_a\) is amorphous density, \(\rho_c\) is crystalline density, and \(\rho\) is density of the film. All values are listed in Table 2.

At 30° C, PEI shows a much lower CO\(_2\) permeability coefficient than PET, even though the crystallinity of the PET film was \(~5\)%, as estimated by DSC (see Figure 5). Table 2 shows that permeability coefficients of PET and PEI films were 4.24 x 10\(^{14}\) and 0.34 x 10\(^{14}\) (cm\(^3\)(STP)/cm\(\cdot\)s\(\cdot\)Pa), respectively, so PET was twelve times as permeable to CO\(_2\) as PEI. Considering the relationship between permeability and crystallinity, completely amorphous PET probably has an even higher permeability than our PET sample. Brolly et al. [12] reported that isotropic PET film (fully amorphous) and biaxially oriented PET film (59% crystalline) had permeabilities of 4\times10^{14} and 3\times10^{14} (cm\(^3\)(STP)/cm\(\cdot\)s\(\cdot\)Pa), respectively. Michael et al. [10] also reported that permeability coefficients for amorphous and crystalline PET films were around 4\times10^{14} and 2\times10^{14} (cm\(^3\)(STP)/cm\(\cdot\)s\(\cdot\)Pa), respectively. Thus permeability can be improved, i.e., lowered, by inducing crystallization, or by drawing and annealing processes. However, the permeabilities reported for crystallized PET are still high, when compared with that of PEI. Actually the permeability of CO\(_2\) in PET is still relatively
low, when compared with other polymers, such as HDPE and PVC. Nevertheless, PEI has a much lower CO$_2$ permeability than amorphous or crystalline PET. This can be considered to be a consequence of differences in their dynamic conformational flexibilities [1]. Amorphous PET is able to freely flip its phenyl rings without changing its overall conformation, but PEI cannot flip its phenyl rings. The flipping of phenyl rings might provide an effective diffusive pathway for gases to permeate through films, and so may account for the greater permeability of CO$_2$ in PET films.
4. CONCLUSIONS

The optimum polymerization conditions to obtain high molecular weight PEI polymers were investigated. PEI can be polymerized with the aid of some catalysts, and their molecular weights can be controlled by varying reaction times and temperatures. Also, when high vacuum is used for the last step of the polymerization, the prepared polymer has a fairly high molecular weight, even at lower reaction temperatures and shorter reaction times. The PEIs prepared here are amorphous polymers, and are difficult to crystallize by heating in the DSC. From gas sorption tests, amorphous PEI film has a much lower CO$_2$ diffusion coefficient (D), solubility coefficient (S), and permeability (P) than does PET. In addition, the monomer for PEI, isophthalic acid, is only slightly more expensive than the terephthalic acid monomer used for PET. Comparing both the permeability and the cost, PEI can be recommended as a potential replacement for PET as a packaging material in certain barrier applications.
5. REFERENCES


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isophthalate) – relationship between physical properties and chemical structures,


Table 1. Reaction conditions and viscosity-average molecular weights for the synthesized PEI samples

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<tr>
<th>Sample #</th>
<th>Temp. (°C)</th>
<th>Time (hr)</th>
<th>Temp. (°C)</th>
<th>Time (hr)</th>
<th>Temp. (°C)</th>
<th>Time (hr)</th>
<th>Vacuum (mm Hg)</th>
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<td>1.5</td>
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Table 2. Density, Crystallinity, and CO$_2$ Diffusion Coefficient, Solubility, and Permeability for PET and PEI

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<th>$\rho$ (g/cm$^3$)</th>
<th>$X_c$ (%)</th>
<th>$M_\infty$ (mg CO$_2$ / g polymer)</th>
<th>$D \times 10^{10}$ (cm$^2$/s)</th>
<th>$S \times 10^5$ (cm$^3$/cm$^3$-Pa)</th>
<th>$P \times 10^{14}$ (cm$^3$/cm-s-Pa)</th>
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<td>1.34</td>
<td>2.24</td>
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<td>0.34</td>
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</table>
Figure 1. The attachment of carboxyl groups to the phenyl rings in PET and PEI
Figure 2. The mechanism for PEI monomer (BHEI) synthesis
Figure 3. The mechanism of the polycondensation reaction for PEI
Figure 4. Typical $^1$H NMR spectrum for PEI samples
Figure 5. Typical DSC thermograms for a commercial PET (upper) and PEI Sample 7 (lower)
Figure 6. WAXD pattern for PEI film
Figure 7. Experimental data for CO$_2$ sorption in PET film at 30° C. The solid line is curve fit obtained from the hybrid-one term method.
Figure 8. Experimental data for CO$_2$ sorption in PEI film (Sample 7) at 30° C. The solid line is curve fit obtained from the hybrid-one term method.
CHAPTER 6. REORGANIZATION OF THE CHAIN PACKING BETWEEN POLY(ETHYLENE ISOPHTHALATE) CHAINS VIA COALESCENCE FROM THEIR INCLUSION COMPOUND FORMED WITH $\gamma$-CYCLODEXTRIN

Amorphous poly(ethylene isophthalate)(PEI) was synthesized, and was used for preparing an inclusion compound (IC) with $\gamma$-cyclodextrin ($\gamma$-CD). Coalesced polymer was produced by washing the PEI-$\gamma$-CD-IC with hot water. Wide angle x-ray diffraction, Fourier transform infrared, and differential scanning calorimetry analyses were employed to verify formation of PEI-$\gamma$-CD-IC and to compare the as-synthesized and coalesced PEI samples. These observations suggested that the structures and morphologies of PEI were changed via coalescence from its $\gamma$-CD inclusion compound. The glass-transition temperature of the amorphous coalesced PEI is 15-20° C higher than the $T_g$ observed for the as-synthesized sample, even when observed in the second heat after cooling from 200° C above $T_g$. While the amorphous as-synthesized PEI retains its randomly-coiling amorphous structure, coalesced PEI has at least partially retained, the highly extended and parallel chains from the narrow channels of the inclusion compound, resulting in better/tighter packing among the PEI chains that manifest a higher $T_g$. 
1. INTRODUCTION

Cyclodextrins are cyclic oligosaccharides obtained by enzymatic digestion of starch (See Figure 1). They consist of six, seven, and eight glucose units linked by 1,4-α-glucosidic bonds for α-, β-, and γ-cyclodextrin, respectively. Their shallow truncated cone shapes make them act as host molecules for the inclusion of both small and long molecule guests, including aromatic esters [1-3], which may lead to the formation of noncovalent, crystalline inclusion compounds. Packing of the CD molecules within the crystal lattice occurs in one of two principal modes (See Figure 1): cage and channel structure [4]. In the cage structure, both ends of the cavity are blocked by adjacent CDs. CDs usually adopt this cage structure in its pure crystal hydrates. In the channel structure the CDs are stacked to form endless columns in the crystal. In polymer-CD inclusion compounds, CD molecules are stacked into the channel structure, and the guest polymer chains are included in the CD columns. Bullions et al. [2] produced poly(ethylene terephthalate) (PET) and bisphenol A polycarbonate (PC) samples by the coalescence of their segregated, extended chains from the narrow channels of the crystalline inclusion compounds formed with γ-cyclodextrin host. They reported that the coalesced PC crystallized in a predominantly chain extended morphology, whereas the coalesced PET crystallized in a chain-folded morphology [2].

In this paper, we investigate the change in the behavior of the usually amorphous polymer, poly(ethylene isophthalate) (PEI), after coalescing from the inclusion compound formed between PEI and γ-cyclodextrin.
2. EXPERIMENTS

2.1. Materials

Poly(ethylene isophthalate) (PEI) was synthesized in our laboratory from pure isophthalic acid (IPA) and ethylene glycol (EG supplied by Amoco and Dupont, respectively. Zinc acetate and antimony trioxide were obtained from Aldrich. $\gamma$-cyclodextrin ($\gamma$-CD) was obtained from Cerestar (Hammond, IN). Trifluoroacetic acid (TFA), chloroform (CLF), and 1,1,2,2-tetrachloroethane (TCE) were all obtained from Aldrich.

2.2 Synthesis of PEI

The synthesis was carried out in two different steps. IPA and EG in a molar ratio of IPA/EG = 1 / 2.5 and the catalysts, zinc acetate (0.15 wt% based on weight of IPA) and antimony trioxide (0.05 wt% based on weight of IPA) were added into a reactor. In the first step, the esterification reaction was conducted at 200º C under nitrogen atmosphere. The reaction mixture was stirred at a constant speed. During the reaction, water was distilled and collected as a byproduct. In the second step (polycondensation), the oligomers, made in the first step, were heated at 222 and 264º C and a vacuum was applied slowly. The condensation reaction was continued for 5 hours. The resultant PEI has a molecular weight of ~ 20,000 g/mole as estimated by its solution viscosity.

2.3. Preparation of PEI-$\gamma$-CD Inclusion Compound (IC)

PEI solution was prepared by dissolution of 0.5g of PEI in 20 ml of solvent (TFA/CLF 1/4 mixture or TCE) at 55º C. The solution was stirred for 45 minutes. A saturated aqueous
solution of $\gamma$-CD was prepared by dissolution of 2 g of $\gamma$-CD in 10 ml of deionized water at room temperature. The $\gamma$-CD solution was slowly added into the PEI solution, and a white gel-like foam formed on top of the liquid mixture. The precipitated mixture was stirred for 3 hours in the 55$^\circ$C oil bath. It was then cooled down to room temperature, allowed to settle for about 24 hours, and was finally vacuum-filtered and dried in a vacuum oven at 50$^\circ$C.

2.4. Preparation of $\gamma$-CD / Solvent Control

1 g of $\gamma$-CD was dissolved in 5 ml of deionized water at 55$^\circ$C. The $\gamma$-CD solution was added dropwise into the solvent (TFA/CLF 1/4 v/v mixture). During the addition, a white foam was formed. The foam was filtered and dried under vacuum at 60$^\circ$C for 15 hours after stirring for 24 hours at 50$^\circ$C.

2.5. Preparation of PEI / Solvent Control

The procedure for PEI- $\gamma$-CD-IC formation was duplicated except that $\gamma$-CD was not dissolved in the deionized water that was added to the TFA/CLF solution of PEI.

2.6. Preparation of Coalesced PEI

Coalesced PEI was obtained by washing the PEI-$\gamma$-CD-IC several times with boiling water over a period of 5 - 6 hours, filtering off the coalesced PEI, and then drying the PEI precipitate under vacuum at 50$^\circ$C.

2.7. Preparation of a PEI / $\gamma$-CD Physical Mixture
A few % of γ-CD were suspended in the TFA/CLF solution of PEI used to make the PEI-γ-CD-IC. This suspension was quickly poured into a large excess of acetone which caused the PEI to precipitate, creating a PEI / γ-CD physical mixture.

2.8. Wide-Angle X-ray Diffraction (WAXD)

WAXD measurements were carried out with a Siemens type-F X-ray diffractometer. A Ni-filtered Cu Kα radiation source (1.54Å) was used for the measurement. The supplied voltage and current were 30 kV and 20 mA, respectively. All specimens were scanned from 2θ = 5 to 30 or 35 ° at a rate of 2θ = 2°/min.

2.9. Differential Scanning Calorimetric (DSC) Analyses

The DSC scans were performed with a PerkinElmer DSC-7 differential scanning calorimeter. The measurements were run from 25 to 260° C at heating and cooling rates of 10° C/min.

2.10. Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectral analyses were carried out in a Nicolet 510P FTIR spectrometer between 4000 and 400 cm⁻¹ with samples in the form of pressed KBr pellets.

3. RESULTS AND DISCUSSION

The minimal cross-sectional dimensions of a PEI polymer chain was approximated as 5.3Å. Thus, though α-CD is likely too small, PEI may fit in both β- and γ-CD hosts (See Figure 1). However the crystalline packing of β-CD in its channel and cage structures is well known to be difficult to distinguish by powder X-ray diffraction [5].
In the case of γ-CD, however, cage and channel structures can easily be distinguished by X-ray diffraction [2]. As a consequence, γ-CD was chosen as the host for PEI in our investigation.

Figure 2 shows wide-angle x-ray diffraction patterns for PEI, γ-CD, and their inclusion compounds. As-synthesized PEI is amorphous as seen in its x-ray pattern, which, though not shown, is virtually identical to the x-ray pattern exhibited by coalesced PEI. Channel-structure inclusion compounds formed by γ-CD are well known to show a strong peak at 2θ = 7.5° in their diffraction patterns, which has been suggested as an indicator for the channel structure [2]. The peak at 2θ = 7.5° is shown clearly in the pattern of PEI-γ-CD-IC obtained with the TFA/CLF solvent system. That means there was almost no free PEI and all polymer chains occupied the narrow cylindrical channels created by the stacks of γ-CD (See Figure 1) in the inclusion compound sample prepared with TFA/CLF solvent. On the other hand, the X-ray pattern of the solid precipitate obtained with TCE does not show the indicator peak. The polymer chains do not occupy the channels of γ-CD, because the γ-CDs are not packed into the channel structure, but rather the cage structure, when using the TCE solvent system. Instead, the narrow cavities of γ-CDs might be occupied by solvent molecules in this case.
Figure 3 shows FTIR spectra for PEI, γ-CD, and their inclusion compound. For γ-CD, the band at 1080 cm$^{-1}$ is contributed by coupled C-C/C-O stretching vibrations, and the band at 1158 cm$^{-1}$ is attributed to the antisymmetric stretching vibration of the C-O-C glycosidic bridge [2]. The PEI-γ-CD-IC obtained from TFA/CLF shows almost the same spectrum as pure γ-CD except for the peak at 1760 cm$^{-1}$, which is assigned to the carbonyl group of PEI. This means PEI and γ-CD make an inclusion compound under the TFA/CLF environment of polymer-IC fabrication. The spectrum for IC-coalesced PEI (spectrum (d) in Figure 3) is almost the same as that of as-synthesized PEI (spectrum (a) in Figure 3), though the small broad peak beyond 3000 cm$^{-1}$ in the spectrum of IC-coalesced PEI might be from the hydroxyl groups of water remaining in the sample. This means that the host γ-CDs were nearly completely removed by washing the inclusion compound with boiling water to coalesce the included PEI.

Changes in the thermal behavior of PEI coalesced from PEI-γ-CD-IC were investigated via DSC. All samples were heated from 25 to 260$^\circ$C and then cooled down to 25$^\circ$C and heated again to 260$^\circ$C. The heating and cooling rates were 10$^\circ$C/min. The DSC curves for as-synthesized PEI are shown in Figure 4. They do not show any melting or crystallization peaks. Both the first heating and second heating scans show glass transition temperatures in the range ~50-55$^\circ$C. The as-synthesized PEI was originally an amorphous material and did not crystallize during heating or cooling at 10$^\circ$C/min. in the DSC (Figure 4). Though not present here, the DSC observations made on the PEI control were virtually identical to the results presented in Figure 4 for as-synthesized PEI.

Figure 5 shows the DSC scans for the PEI sample obtained by hot water coalescence from PEI-γ-CD-IC. The first heating curve (a) shows a glass transition and a very small
endothermal peak at 70 and 120º C, respectively, with a heat of fusion (ΔH) of 0.467 J/g for
the endothermal peak. The cooling curve [Figure 5 (b)] shows what appears to be a small,
broad crystallization peak at ~ 65º C. The second heating curve [Figure 5 (c)] shows only a
glass transition temperature at virtually the same temperature as observed in the first heating.
The small endothermic peak observed at 120º C in the first heat of coalesced PEI may be
attributed to the vaporization of residual moisture in the sample, because, though not shown,
a similar small endotherm was observed in the DSC scan of the PEI/γ-CD physical mixture.
The glass transition temperature of coalesced PEI is ~15-20º C higher than that of the
as-synthesized PEI, though both appear completely amorphous. The glass transition shifted
to a higher temperature after the inclusion in and coalescence from its inclusion compound
with γ-CD. Usually polymer chains in amorphous regions start to move at the glass transition
temperature. The coalesced PEI chains only begin to move at a temperature significantly
higher than as-synthesized PEI chains, probably because the coalesced PEI chains are
extended and their packing is more orderly than in the as-synthesized totally amorphous PEI
with its randomly coiling chains. The greater extension and tighter packing of coalesced PEI
chains apparently remains even after heating to 200º C above Tg, because nearly identical
elevated Tgs are observed during the first and second DSC heating scans.
The process of coalescing PEI from its inclusion compound with γ-CD has resulted in the
extension and parallelization of PEI chains during the formation of the inclusion compound
which do not completely disappear after the removal of γ-CD by washing with hot water and
coalescence of the PEI chains. A schematic representation of our view of the formation of
and coalescence from PEI-γ-CD-IC is shown in Figure 6. The 15 – 20º C elevation in Tg of
amorphous PEI produced by inclusion in and coalescence from PEI-γ-CD-IC is significant.
4. CONCLUSIONS

PEI, its inclusion compound with $\gamma$-CD, and PEI coalesced from the IC were produced and characterized. The $T_g$ exhibited by the amorphous coalesced PEI is substantially higher (~15-20° C) than that of the as-synthesized PEI, even during the second heating of the coalesced sample. These observations are consistent with the completely amorphous, randomly-coiling and the more extended and parallel, less randomly-coiling natures of PEI chains in as-synthesized and coalesced samples, respectively.

5. REFERENCES


Figure 1. Structures and molecular dimensions of α-, β-, and γ-cyclodextrins (Top) and cyclodextrin crystal structures (Bottom)
Figure 2. WAXD results for PEI samples: (a) as synthesized PEI, (b) $\gamma$-cyclodextrin, and PEI-$\gamma$-CD inclusion compounds prepared in (c) tetrachloroethane and (d) in trifluoroacetic acid/chloroform mixed solvent.
Figure 3. FTIR spectra of (a) as-synthesized PEI; (b) γ-cyclodextrin; (c) PEI-γ-CD-IC; and (d) coalesced PEI.
Figure 4. DSC scans for as-synthesized PEI; (a) first heating, (b) cooling, and (c) second heating.
Figure 5. DSC scans for coalesced PEI; (a) first heating, (b) cooling, and (c) second heating.
Figure 6. Schematic representation of polymer chain packing controlled by the formation of and subsequent coalescence from its CD-inclusion compound.
CONCLUSIONS

Poly(ethylene terephthalate) (PET) is used worldwide for the production of synthetic fibers, films, beverage bottles, and molded plastic parts, because of its good physical properties. Poly(trimethylene terephthalate) (PTT) was commercialized very recently. However, poly(ethylene isophthalate) (PEI) and poly(trimethylene isophthalate) (PTI), structural isomers of PET and PTT are relatively unexplored polymers. There have been few studies reported on the polymerization, spinning, and characterization of those two polyesters. PEI and PTI have almost the same chemical structures as PET and PTT, respectively. The only difference is PEI and PTI have carbonyl groups attached in the 1,3-meta positions of its phenyl rings instead of the 1,4-para positions. These polyesters, PET, PTT, PEI, and PTI were manufactured by condensation polymerization. The PEI prepared in lab scale polymerization was amorphous and it did not have any crystallization peak and melting peak in DSC analysis. Amorphous PEI film had a much lower CO₂ diffusion coefficient (D), solubility coefficient (S), and permeability (P) than does PET. This is because in PET the phenyl rings are substituted in the para (1,4) positions, which allows for their facile flipping, effectively permitting gases to pass through. However, the meta-substituted phenyl rings in PEI do not permit such ring flipping, and thus PEI may be more suitable for barrier applications.
PEI inclusion compound (IC) with $\gamma$-cyclodextrin and coalesced PEI from the IC were produced and characterized. $T_g$ of the amorphous coalesced PEI was substantially higher (~15-20°C) than that of the as-synthesized PEI, even after the second heating of the coalesced sample. These observations are consistent with the completely amorphous, randomly-coiling and the more extended and parallel, less randomly-coiling natures of PEI chains for as-synthesized and coalesced samples, respectively.

PET, PTT, PEI, and PTI were also prepared in 1-gallon Parr reactor by condensation polymerization. The condensation reaction temperatures were 260 ~ 285°C under low pressure, 0.4 ~ 0.6 torr. The polymerization reactions for PEI and PTI were slower than for PET and PTT with the same amount of catalysts. The molecular weights were 28,300, 33,300, and 17,800 g/mole for PET, PTT, and PEI, respectively. The intrinsic viscosity of PTI was 0.54 dL/g. In DSC analysis, PET, PTT, PEI, and PTI show $T_g$’s at 71, 48, 54, and 43 °C. PET and PTT show $T_{cc}$’s at 144, and 69 °C, and $T_m$’s at 253 and 228 °C, respectively. PEI shows $T_g$ at 54 °C, and $T_{cc}$ and $T_m$ at 176, and 243 °C, but areas of these peaks are relatively small. PTI has $T_g$ at 45° C, but it does not have a $T_{cc}$ or $T_m$. In the case of PEI, it formed different kinds of crystals with different melting points depending on the crystallization methods. The crystals formed by annealing or orientation show a high melting temperature at around 240° C, while the crystals formed from solution by slow evaporation
show a low melting temperature at around 124° C. All the synthesized polyesters show high thermal stability in TGA analysis. The peak temperatures (T_{max}) of the maximum rate of mass loss were 505, 463, 475 and 426° C for PET, PTT, PEI, and PTI respectively. PET and PTT were melt-spun with Fourne single screw extruder with several take-up speed, from 2500 ~ 4500 m/min. The PTT fiber had a higher strain and lower tenacity than PET fiber. PEI and PTI were melt-spun with Bradford piston type extruder, and these fibers were very uneven and weak. PEI fiber was white, and PTI fiber was transparent.

Usually polymers prepared by condensation polymerization contain cyclic molecules along with the linear chains. Conventionally produced polyesters also contain small amounts of cyclic low molecular weight oligomers. We investigated ring-opening polymerization of the cyclic oligomers. The ring-opening polymerization offers potential advantages relative to the conventional polymerization process. It does not produce any small molecule by-product and the reaction can be carried out at atmospheric pressure. Also, a low melt viscosity of the cyclic oligomers allows processing by various techniques such as pultrusion, resin-transfer molding, melt filtration, or reaction injection molding either concurrent with or just prior to polymerization. Cyclic dimer of PTT (TTC), collected as a byproduct in the PTT manufacturing process, was polymerized to linear PTT. The TTC dimer is produced during manufacturing and collected and thrown away because it adversely affects polymer’s
physical properties. In this dissertation we discovered and report that the by-product, cyclic oligomer can be converted to a linear polymer by the ring opening polymerization with catalysts. The polymerization was carried out with a round bottom reactor, and antimony(III) oxide, titanium(IV) butoxide, dibutyltin oxide, and titanium(IV) isopropoxide were used as catalysts. The highest molecular weight was 40,000 when 0.25 mol% of titanium(IV) butoxide was used as a catalyst.

The cyclic oligomers can be deliberately synthesized and used as a feedstock for the ring-opening polymerization. Cyclic oligomers of PET, PTT, PEI, and PTI were synthesized by cyclo-depolymerization of linear polymer; PET, PTT, PEI, and PTI. The PET cyclic oligomer (CDP-ETC) and PTT cyclic oligomer (CDP-TTC) were mixtures of several sized oligomers including mainly trimer and dimer based on HPLC analysis. The structures were cyclic in form as confirmed by FTIR. The melting temperatures were 59, 122, 194, and 276 °C for CDP-ETC, 241 °C for CDP-TTC, 335 °C for CDP-EIC, and 147 °C for CDP-TIC. CDP-ETC, CDP-TIC, and CDP-EIC could be polymerized without catalyst during 5 minutes in the DSC, but CDP-TTC could not be converted into a polymer. The cyclic oligoesters were polymerized in the reaction tube with antimony(III) oxide as a catalyst. The molecular weights of ROP polymers were 3000 g/mol of PET, 4900 g/mol for PTT, and 7200 g/mol for PEI. The intrinsic viscosity of ROP-PTI was 0.25 dL/g. The ROP polyesters show very
similar thermal properties with the regular industrial polyesters, even though their molecular weights were not as enough.