SCREENING OF VARIOUS POLYETHYLENE TEREPHTHALATE CHAIN EXTENDERS IN A MELT POLYMERIZATION SET-UP

by
Ayşenur Özdemir
B.S., Chemistry, Boğaziçi University, 2013

Submitted to the Institute for Graduate Studies in
Science and Engineering in partial fulfillment of
the requirements for the degree of
Master of Science

Graduate Program in Chemistry
Bogazici University
2015

Dedicated to My Parents, Grandma and to

The Memory of Bedi Hoca

ACKNOWLEDGEMENTS

Firstly, I would like to thank my supervisor Assoc. Prof. Ali Ersin Acar for accepting me his research group almost 5 years ago. It is a pleasure for me to express my sincerest gratitude to him for his guidance, support, encouragement and patience throughout these years.

I would like to thank my committee members Prof. Duygu Avcı Semiz and Assoc. Prof Alpay Taralp for giving their valuable time for reviewing my thesis.

During these 5 years I have been working with lots of precious people. Firstly, I would like to thank Ahmet, Turhan, Sezgin, Şükrü and Nurdan for their help, guidance and friendship. It was a wonderful chance for me to work with them when I was a research student. I owe a lot to my friends Halenur, Kâmil, Duygu, Sedef, Seda, Aylin, Didem and Işıl. Without their help, friendship and smile, these two years would not be full of laugh. Especially I would like to thank Kâmil for his help during my experiments. They made all the hard times easier and enjoyable. Also, I would like to thank, Gökçe, Cem, Elif, İlknur and Turgay for their friendship. Once again I would like to thank all the people I work with in Acar Lab for their friendship.

I would like to thank my dearest friends Damla, Elif, Ezgi and Mina for their friendship, support and all the amazing memories we had over almost 20 years. Also, I would like to thank Sena and Mehtap for their friendship and encouragement. I am so much grateful that they are in my life. I would like to thank Ayça for her enjoyable friendship, help and sharing her home with me while I was writing this thesis. I owe a lot to Efsane who did not leave me alone during hard times and gave me all her positive energy to move on. It would be unfair if I forget to thank all the amazing people I met at the chemistry department, Ekmel, Çimen, Sinem, Ari and Elif for their friendship. Last but not the least I would like to thank my beautiful friend Ece for her encouragement, support, patience to me and her enjoyable friendship. Life would be too boring without her.

This thesis would not have been possible without my family. I would like to thank my aunties Fevziye and Nur and also my cousin Deste for their support throughout my life.

Finally, my sincere thanks go to my parents for their love, trust, support, encouragement and belief in me. I cannot imagine a better childhood and home.

ABSTRACT

SCREENING OF VARIOUS POLYETHYLENE TEREPHTHALATE CHAIN EXTENDERS IN A MELT POLYMERIZATION SET-UP

Polyethylene terephthalate (PET) is one of the most important and common polyester in the industry. It is produced by the reaction of ethylene glycol (EG) with terephthalic acid (TPA) or dimethyl terephthalate (DMT). The polymerization can be carried out through melt then, if high molecular weights are targeted, solid state polymerization. PET has excellent chemical resistance, high mechanical strength and high thermal stability. Therefore it is used in very different application areas. For every application area PET have different molecular weight values. As the molecular weight requirement increases the production of PET becomes difficult *via* melt polymerization. Solid state polymerization (SSP) is used for high molecular weight PET production. SSP's disadvantage is that reaction time is very long and therefore expensive. Also, during processing of PET, molecular weight decreases because of the heat applied. All these problems can be addresed *via* chain extenders. In this study, chain extension reactions of PET with four different chain extenders, carbonyl biscaprolactam, 1,3-phenylene-bis-oxazoline, DE and SO were carried out and their effect on molecular weight were investigated. Structures of DE and SO will not be noted in this thesis due to the confidentiality of the study.

ÖZET

ÇEŞİTLİ POLİETİLEN TEREFTALAT ZİNCİR UZATICILARININ ERİYİK POLİMERLEŞME SİSTEMİNDE İNCELENMESİ

Polietilen tereftalat endüstride kullanılan en önemli ve yaygın poliesterdir. PET, etilen glikolün tereftalik asit ya da dimetil tereftalat ile olan reaksiyonları ile sentezlenmektedir. Eriyik ya da katı hal polimerleşmesi ile moleküler ağırlığı arttırılmaktadır. PET ‘in yüksek ısı, kimyasal ve mekanik dayanıklılığı olması dolayısıyla farklı kullanım alanları mevcuttur. Ancak farklı kullanım alanları için PET ‘in farklı moleküler ağırlıklarda olması gerekmektedir. İstenilen moleküler ağırlık değeri arttıkça, eriyik polimerleşme ile PET sentezi zorlaşmaktadır. Bundan dolayı yüksek moleküler ağırlıktaki PET sentezi için katı hal polimerleşme metodu kullanılmaktadır. Uzun reaksiyon süresi sebebi katı hal polimerleşmesini pahalı bir metod haline getirmektedir. Ayrıca PET ‘in işlenmesi süresi boyunca da uygulanan ısı ve basınçtan dolayı moleküler ağırlığı azalmaktadır. Bütün bunlara çözüm olarak zincir uzatıcı maddeler kullanılmaktadır. Bu çalışmada PET ’in dört farklı zincir uzatıcı ile gerçekleştirilen zincir uzatma reaksiyonları ile bunların PET ‘in moleküler ağırlığı üzerindeki etkisi araştırılmıştır.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS iv

ABSTRACT vi

ÖZET vii

LIST OF FIGURES x

LIST OF TABLES xii

LIST OF ACRONYMS/ABBREVIATIONS xiii

1. INTRODUCTION 1
   - 1.1. Polyethylene Terephthalate 1
   - 1.2. Application Area 2
   - 1.3. Melt Polymerization of PET 4
   - 1.4. Solid State Polymerization 7
   - 1.5. PET Degradation 8
   - 1.6. Chain Extension 11
     - 1.6.1. Chain Extenders 13
     - 1.6.2. Methods For Chain Extension 16

2. AIM OF THE STUDY 18

3. EXPERIMENTAL 19
   - 3.1. Chain Extension Reactions of PET 19
   - 3.2. Gel permeation chromatography (GPC) Analysis 20
   - 3.3. Intrinsic Viscosity (IV) Analysis 20
   - 3.4. Carboxyl End Group Analysis 20

4. RESULTS AND DISCUSSION 21
   - 4.1. PBO and DE Effects on IV-CEG of PET. 21
   - 4.2. CBC and SO Effect on IV-CEG of PET 24
   - 4.3. Chain Extenders Effect on Molecular Weight of PET. 27

5. CONCLUSIONS 31

6. FUTURE WORK 32

REFERENCES 33

LIST OF FIGURES

Figure 1.1. Repeating Unit of PET's Structure. 1

Figure 1.2. PET Production Capacity [9]. 3

Figure 1.3. Synthesis Route for PET. 5

Figure 1.4. Thermal Degradation Mechanism of PET. 8

Figure 1.5. DEG Formation [2, 6]. 9

Figure 1.6. Dioxane Formation. 9

Figure 1.7. Cyclization of PET [2]. 9

Figure 1.8. Hydrolytic Degradation of PET. 10

Figure 1.9. Thermooxidative Degradation of PET [23]. 11

Figure 1.10. General Mechanism of Chain Extension. 12

Figure 1.11. Reaction of PET with Bisoxazoline. 13

Figure 1.12. Reaction Mechanism of PET with Carbodiimide. 14

Figure 1.13. Reaction of PET with Diepoxide. 14

Figure 1.14. Reaction Mechanism of PET with Dianhydride. 15

Figure 1.15. Reaction Mechanism of PET with Diisocyanate. 16

Figure 4.1. 1,3-Phenylene-bis-oxazoline. 21

Figure 4.2. Reaction Mechanism of PET with 1,3-Phenylene-bis-oxazoline. 22

Figure 4.3. Diepoxide Structure. 22

Figure 4.4. Reaction mechanism of PET with Diepoxide. 23

Figure 4.5. Carboxyl End Group Concentration *versus* Mol of Chain Extenders........ 23

Figure 4.6. Intrinsic Viscosity *versus* Mol of CE.. 24

Figure 4.7. Carboxyl End Group Concentration *versus* Mol of CE. 24

Figure 4.8. Carbonyl Biscaprolactam... 25

Figure 4.9. Reaction Mechanism of PET with Carbonyl Biscaprolactam..................... 25

Figure 4.12. Intrinsic Viscosity *versus* Mol of CE.. 26

Figure 4.13. Carboxyl End Group Concentration *versus* Mol of CE. 26

Figure 4.14. Carboxyl End Group Concentration *versus* Intrinsic Viscosity................. 27

Figure 4.15. PDI *versus* Mn. 28

Figure 4.16. CEG *versus* Mn.. 29

Figure 4.17. Mw *versus* IV.. 30

LIST OF TABLES

Table 1.1. Physical Properties of PET. 2

Table 1.2. IV Values of PET According to Application Areas [10]. 4

Table 3.1. Stoichiometries of reactions. 19

LIST OF ACRONYMS/ABBREVIATIONS

CBC	Carbonyl Biscaprolactam
CE	Chain Extender
CEG	Carboxyl End Group
COOH	Carboxylic Acid
COOMe	Methyl Acetate
DE	Diepoxide
DEG	Diethylene Glycol
DMT	Dimetyl Terephthalate
EG	Ethylene Glycol
HFIP	Hexafluoroisopropanol
ICI	Imperial Chemical Industries
IV	Intrinsic Viscosity
Mn	Number Average Molecular Weight
Mw	Weight Average Molecular Weight
OH	Alcohol
PBO	Phenyl Bisoxazoline
PDI	Polydispersity Index
PET	Poly (ethylene terephthalate)
SO	Novel Chain Extender

SSP	Solid State Polymerization
Tg	Glass Transition Temperature
Tm	Melting Temperature
TPA	Terephthalic Acid

1. INTRODUCTION

1.1. Polyethylene Terephthalate

Polyesters which have the largest part in the synthetic polymer world are produced *via* step-growth condensation reactions using difunctional monomers [1-3]. The most important polyester in synthetic polymer world is poly (ethylene terephthalate) (PET) that is a partly aromatic polyester. PET is synthesized by aliphatic diols and aromatic carboxylic acids or esters [1, 4]. Around 1946-1948 PET is developed in commercial grade in England as Terylene and in USA as Dacron but it is fabricated first time by Imperial Chemical Industries (ICI) [3]. In 1953, Dupont made fiber from PET [1].

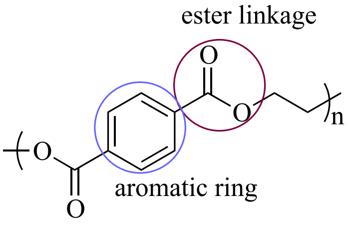

Figure 1.1. Repeating Unit of PET's Structure.

PET is a thermoplastic, semi-crystalline, aromatic polyester [1, 2]. The repeating unit of PET is shown in Figure 1.1. Due to the short ethylene groups and aromatic groups in the backbone of the polymer, mobility of the PET chains decrease. This makes PET chains pack together well therefore PET has high crystallinity. High crystallinity makes PET chemically resistant and tough. Also, due to chain properties mentioned above PET has excellent mechanical strength, processability, thermal stability (Table 1.1) and colour ability [5, 6].

Table 1.1. Physical Properties of PET.

Property	Value
Glass Transition Temperature (°C) (T_g)	69 - 115
Melting Temperature (°C) (T_m)	250 - 265
Crystallization Temperature (°C)	150 - 190
Breaking Strength (Mpa)	50
Tensile Strength (Young's Modulus) (Mpa)	1700
Yield strength (%)	4
Impact Strength ($J\ m^{-1}$)	90
Permeability to hydrogen at (25 $cm^3.cm\ cm^{-2}s^{-1}Pa^{-1}$)	0.4×10^{-13}
Permeability to nitrogen at (25 $cm^3.cm\ cm^{-2}s^{-1}Pa^{-1}$)	0.004×10^{-13}
Permeability to oxygen at (25 $cm^3.cm\ cm^{-2}s^{-1}Pa^{-1}$)	0.03×10^{-13}

1.2. Application Area

PET has excellent heat resistance, gas barrier values, mechanical strength and chemical resistance [7]. Because of these physical and chemical properties PET is the most important thermoplastic in the industry [8]. Its application areas increase over the years. The increase in the production amount of PET can ben seen in Figure 1.2.

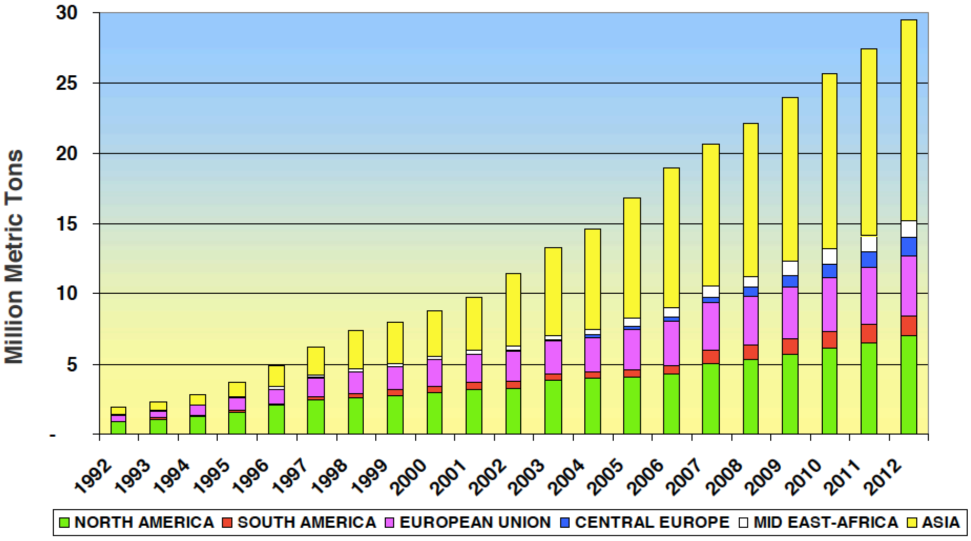

Figure 1.2. PET Production Capacity [9].

PET is mostly used for fiber production but low gas barrier values and good chemical resistance make PET usable for beverages bottles [7, 10]. Also, it is used for photographic films, audio/video tapes and packaging films even as electrical insulating material for capacitors [7, 11, 12].

Every application area needs different molecular weight PET. For example low carboxylic acid end group (CEG) makes PET more thermally and hydrolytically stable, high molecular weight PET is though and chemically stable [13]. Table 1.2 shows the application areas of PET according to intrinsic viscosity (IV) values. The correlation between IV and molecular weight comes from Mark-Houwink equation.

Table 1.2. IV Values of PET According to Application Areas [10]

Application Area	IV (dl/g)
Textile	0.40 - 0.70
Technical	0.72 – 0.98
Biaxially oriemted film	0.60 – 0.70
Sheet grade for thermoforming	0.70 - 1.00
Water Bottle	0.70 – 0.78
Carbonated soft drink grade	0.78 - 0.85

1.3. Melt Polymerization of PET

Polymerization process which takes place above the melting points of monomers and polymer is defined as melt polymerization [14].

For PET production there are two steps in melt polymerization. The first step is the synthesis of the oligomers and the second step is the polycondensation reactions where oligomers and prepolymers merge with each other [15].

PET synthesis can take place *via* two different reaction routes that can be seen in Figure 1.3. One reaction is esterification where terephthalic acid (TPA) reacts with ethylene glycol (EG) and forms bis-hydroxy ethylene terephthalate (BHET) and short oligomer chains reacts again and the by-product is water. The other reaction is the transesterification whose difference from the first method is the use of dimethyl terephthalate (DMT) instead of TPA [2, 4].

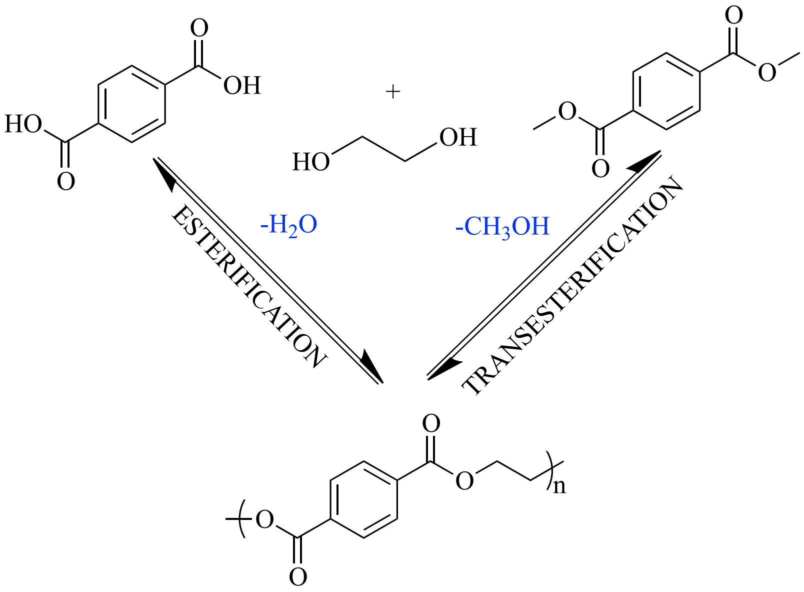

Figure 1.3. Synthesis Route for PET.

There are some differeneces between esterification reaction and transesterification reaction, which affect the overall synthesis of PET. Transesterification reactions need metal acetate catalysts like Zn, Mn, Cd, Pb, Ca, Mg whereas in esterification reactions TPA’s acid functionality may catalyze the reaction [2, 15]. TPA route produces water as by product beside EG. DMT pathway produces methanol instead of water. Even though methanol is more volatile and accelerates the reaction according to Le Chatelier's principle, handling water is easier [2]. Also, carboxyl end group PET is more favorable in industry. Another important difference between TPA and DMT usage is that TPA does not melt in EG so homogenous mixing is very important for esterification reaction [10]. Diethylene glycol (DEG) formation occurs initial stages of polycondensation step but this amount is higher for esterification reactions because TPA’s higher acidity increases DEG formation [4]. The disadvantages of DEG formation in PET synthesis will be explained in detail at the following degradation Section 1.6.

Once oligomers are synthesized, second stage of PET synthesis is the polycondensation reaction between BHET’s and prepolymers [2]. During the polycondensation stage, oligomers’ -OH and -COOH or- COOMe end groups give polycondensation reactions and molecular weight of PET increases to the desired level depending on the application area [10].

Even though -COOH groups of TPA catalyzes the reaction, it is not possible to produce commercial PET without any catalyst because the reaction time is too long. When the time increases and PET is exposed to high temperature, the extent of thermal degradation increases [2]. Sb, Ti, Ge, Sn Metals compounds can be used as polycondensation catalysts [16]. Generally antimony trioxide is used for PET synthesis at the polycondensation step [15]. The catalyst amount used differs from 0.05% to 0.1% by weight with respect to the DMT or TPA [10].

In the literature, there are different reaction conditions for the melt polymerization of PET. Temperature profile changes from 150 to 210 ^{o}C for first step and from 260 °C to 290 °C for polycondensation step with vacuum value 0.5-1 torr or 0.13 KPa [4,10,15,16]. Vacuum is applied to remove EG from medium at the polycondensation step.

As the reaction proceeds, the melt viscosity of PET increases. When viscosity and chain lengths start increasing, it gets harder for -OH and COOH or -COOMe groups to find each other. To decrease the melt viscosity reaction temperature is increased. This results in decrease at the condensation rate and as a result reaction becomes diffusion controlled [17].In contrast, degradation rate increases because of long reaction time at high temperatures (higher than PET's melting point) [10].

The products that are formed during degradation process like DEG and acetaldehyde (AA) affect the excellent mechanical, thermal and chemical properties of PET. Also, a high amount CEG concentration, which is the result of degradation reactions, makes PET thermally and hydrolytically unstable. Degradation reactions will be explained in detail at Section 1.6. Increased IV value starts decreasing due to degradation reactions. Therefore melt polymerization is not an appropriate method for PET production whose IV value is higher than 0.7 dl/g [10].

In other words, melt polymerization can be used for low IV PET production but to increase IV and overcome the melt polymerization problems solid state polymerization method is used [6, 11].

1.4. Solid State Polymerization

The polymer that has IV value lower than 0.7 dl/g can be produced by melt polymerization as mentioned above. For polymers that require higher IV values and toughness solid state polymerization (SSP) is the only efficient solution that overcomes theproblems encountered in melt polymerization [18, 19].

SSP is an effective method to increase the molecular weight of polymer [20]. It differs from melt polymerization at the temperature profile. In melt polymerization, monomers and polymers are in molten state. In contrast, at SSP everything is in solid state. Reaction temperature is lower than the Tm of the used polymer but higher than the Tg of the polymer [6].

The temperature profile changes from 200 °C to 240 °C for SSP of PET. Also vacuum is applied to system to remove the by-products. Reaction time varies from 5 hours to 25 hours [5]. System is under nitrogen [4].

Prepolymers from melt polymerization are used at SSP. Before SSP, prepolymers are crystallized at temperatures higher than the polymer's Tg. Chain mobility increases during this process at amorphous parts of the polymer [4]. Also, the moisture in the prepolymers is decreased and this results in minimum hydrolytic degradation. Thermal degradation and DEG formation are minimized due to the lower temperature profile of SSP [21]. At the end PET's IV value can be enhanced to 1 dl/g or even higher.

In brief, SSP is used to obtain high molecular weight PET. It eliminates the disadvantages of melt polymerization.

On the other hand this method requires special equipments like special heaters, hopper driers, hopper reactors and its reaction time is very long [4, 22]. To overcome these disadvantages, another method is introduced which is the chain extension reactions [10]. They will be explained in detail in Section 1.6.

1.5. PET Degradation

PET is a polymer that is unaffected by almost all organic compounds and especially acids [23]. Also, PET is thermally very stable. However, at temperatures higher than its melting point its molecular weight decreases and CEG concentration increases. This implies that during the melt polymerization and processing of PET, degradation reactions take place [17].

There are mainly three factors which causes chain scissions at temperatures between 270°C - 300°C, heat, moisture and oxygen [17]. For all type of degradations thermal energy is needed.

The main degradation reaction is thermal degradation whose mechanism is shown in Figure 1.4.

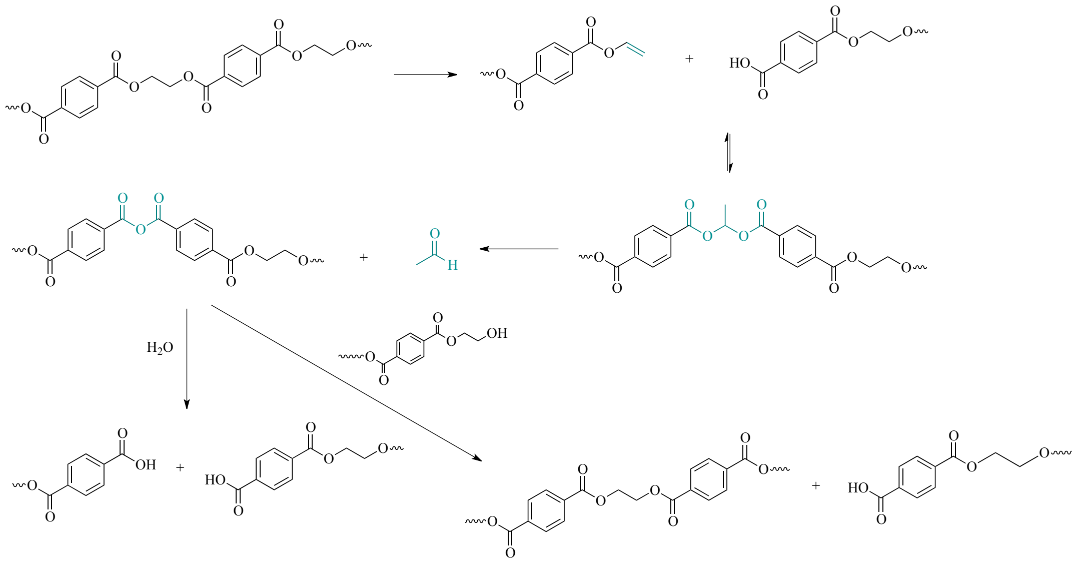

Figure 1.4. Thermal Degradation Mechanism of PET.

The thermal degradation of the ester bond forms vinyl ester at the first stage. Then reaction proceeds and then acetaldehyde (AA) is formed [4]. Extent of degradation is often measured by CEG tests but it can also be measured from AA concentration. The amount of AA is important for food packaging. In PET, AA concentration must be lower than 1 ppm because of its ability to contaminate the drinks or food [4].

Other thermal degradation reactions results in DEG and dioxane formation and cyclization of PET as shown in Figure 1.5, Figure 1.6, Figure 1.7 respectively.

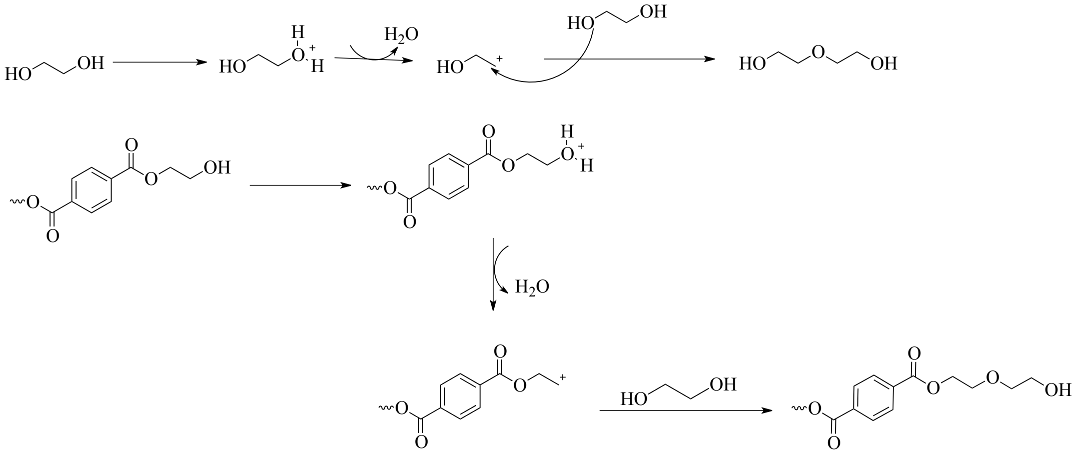

Figure 1.5. DEG Formation [2,6].

DEG is formed *via* etherification reactions of EG with -OH end groups of PET chains or reaction between EG's. Incorporation of the DEG to the backbone increases the overall chain mobility in PET, and this results in lower melting points. Dioxane is the other degradation product. Its formation depends on the DEG concentration in the reaction. Dioxane is more volatile then DEG. It is removed from reaction medium by vacuum [4].

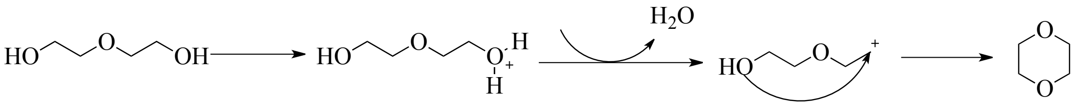

Figure 1.6. Dioxane Formation.

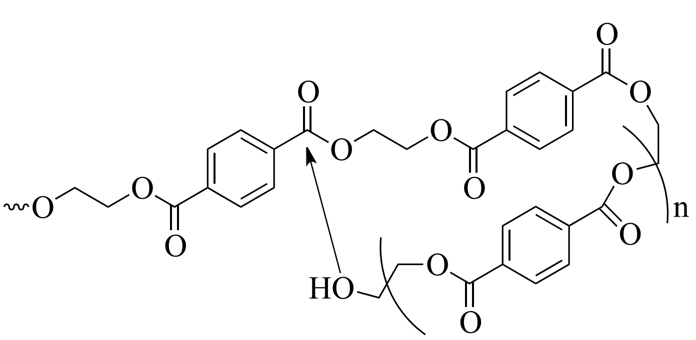

Figure 1.7. Cyclization of PET [2].

Briefly thermal degradation reactions shorten the polymer chains, produce side products and increase the CEG concentration. High CEG concentration decreases the hydrolytic stability of PET [19]. In Figure 1.7. hydrolytic degradation of PET is shown. It can be seen that as the polymer chains shorten the CEG concentration increases.

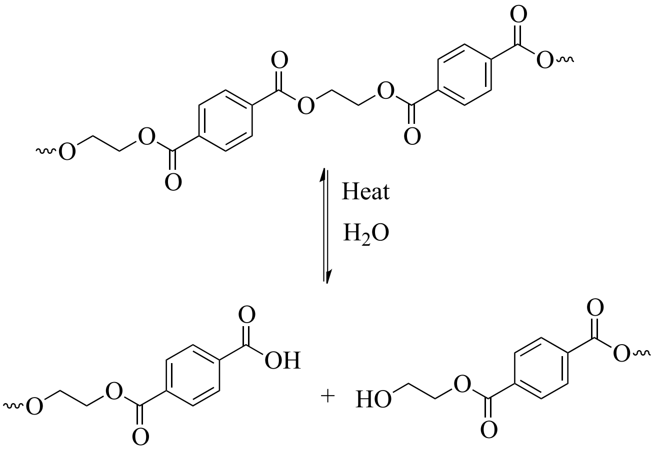

Figure 1.8. Hydrolytic Degradation of PET.

The third degradation mechanism is a thermooxidative one, which is induced by heat and oxygen (Figure 1.8.) This degradation mechanism is the one that is responsible from crosslinkings and gelation of PET [17].

In brief, PET undergoes chain scission reactions at high temperatures. Moisture and oxygen in the medium accelerate the degradation reactions and creates other side products. Natural outcome of all degradation reactions are decrease in molecular weight and increase in CEG concentration.

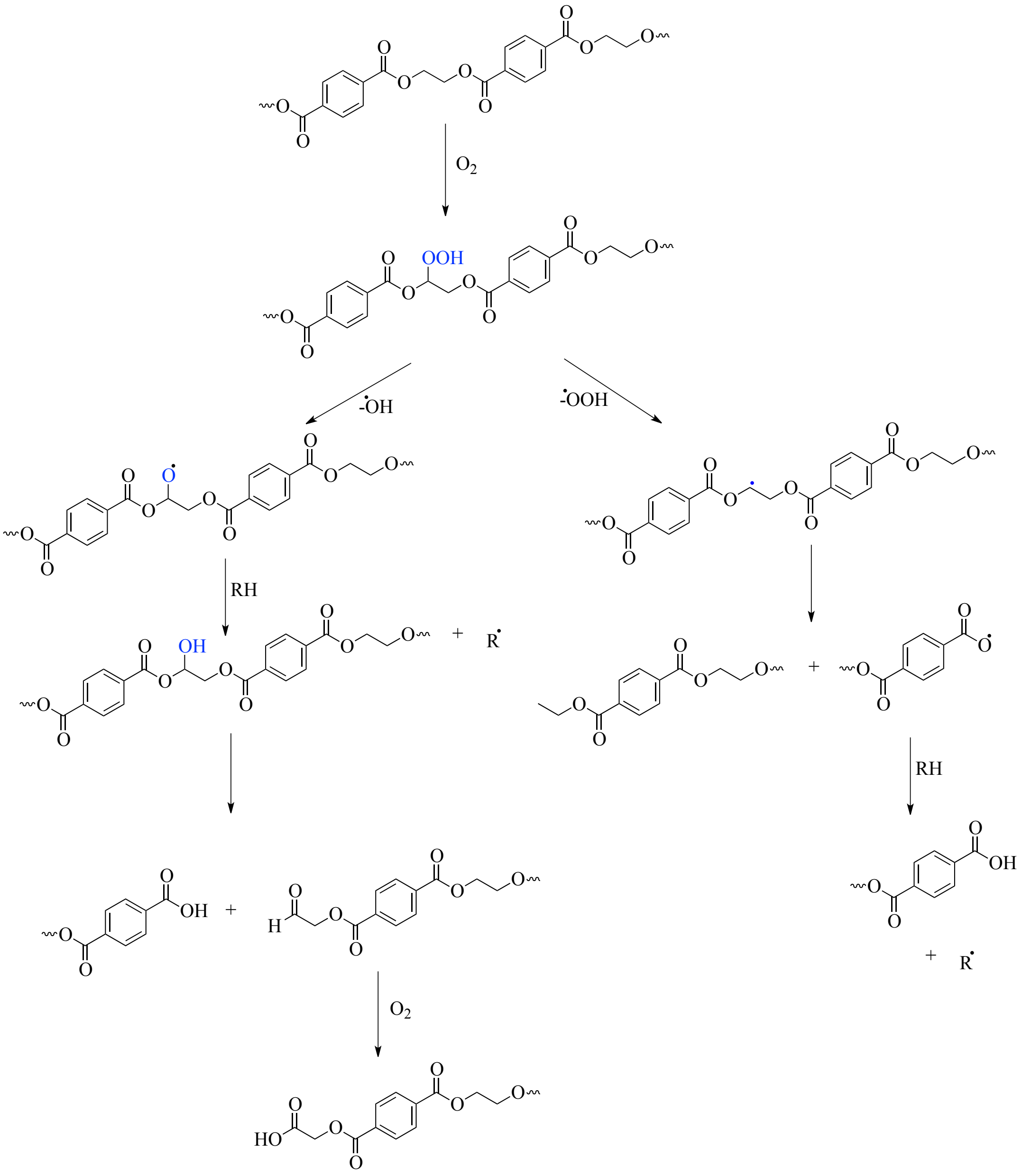

Figure 1.9. Thermooxidative Degradation of PET [23].

1.6. Chain Extension

During the processing of PET, chain scissions may occur which decreases the molecular weight [5]. Chain extenders are often used to compensate the molecular weight drop and increase the melt strength of the polymer [11, 24].

Chain extension term is used for reactions where polymer chain end groups react with di- or multi-functional organic compounds or low molecular weight polymers [5, 25]. The general approach in chain extension is shown in Figure 1.6 where the red balls are end groups of polymer chains and green ball is a chain extender. Reaction between the polymer end groups and the chain extenders are picked among fast reactions [18].

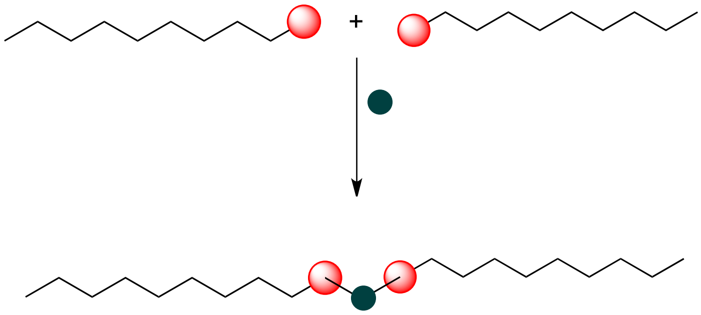

Figure 1.10. General Mechanism of Chain Extension.

In PET case, chain extension reaction occur between OH or COOH end groups of PET and the chain extenders [26].

When PET chains end groups come across with chain extenders, there are three possibilities:

(i) Chain extenders one side reacts with one end group of PET and reaction stops in other words, CE blocks the polymer chain.

(ii) Chain extenders combine two PET chain and enhance the molecular weight. This is what is generally aimed.

(iii) Chain extender does not give reaction with PET's end groups [5].

At the end of the chain extension reactions, molecular weight increases and polymer has new physical and chemical properties depending on the type and amount of the CE [25].

1.6.1. Chain Extenders

The chain extenders are bi-or multi-functional compounds which react with polymer end groups and form new covalent bonds [27, 28].

Chain extenders should be thermally stable and have reactive sides towards the polymer end groups. Most of the chain extenders forms by-products after reactions with polymers [27] If by-products boiling points are high, their removal gets harder and this makes those chain extenders less favorable [19]. In chain extension reactions which occur *via* ring opening reactions, no by-product is formed [29].

In the case of PET, chain extenders should be reactive towards -OH or COOH end groups [19]. The most common chain extender types used for PET are diepoxides, dianhyrides, bisoxazolines, carbodiimides, diisocyanates, bis-dihydrooxazines [22, 30]

The reaction mechanisms of PET with these common chain extenders can be seen in the figures below.

Bisoxazolines are -COOH group reactive compounds. They give ring opening reaction with PET. By-products are not formed. PET chains include amide bonds after the chain extension reaction.

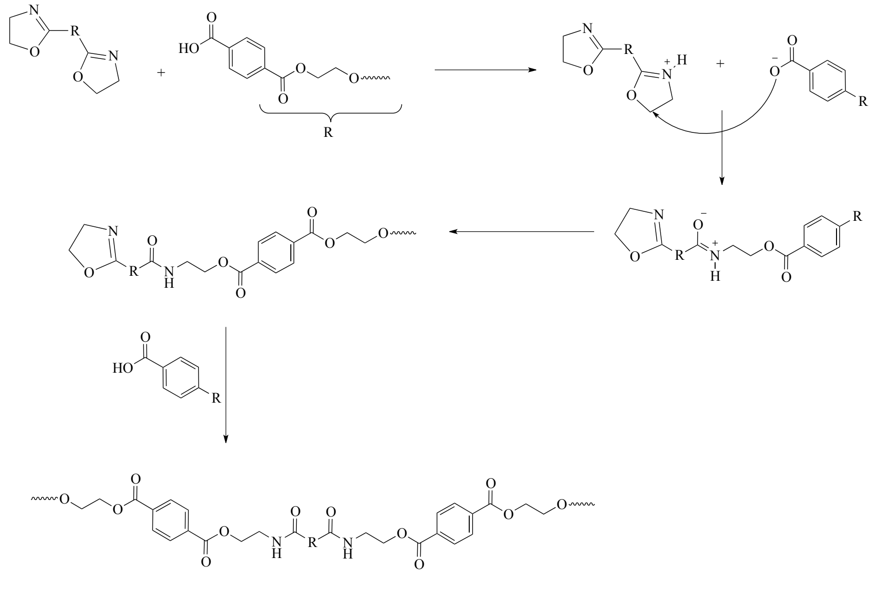

Figure 1.11. Reaction of PET with Bisoxazoline.

Carbodiimides are OH group reactive compounds. They form urea as by-product (Figure 1.12). At intermediate step anhydride is formed but alcohol end groups of PET breaks the anhydride bond

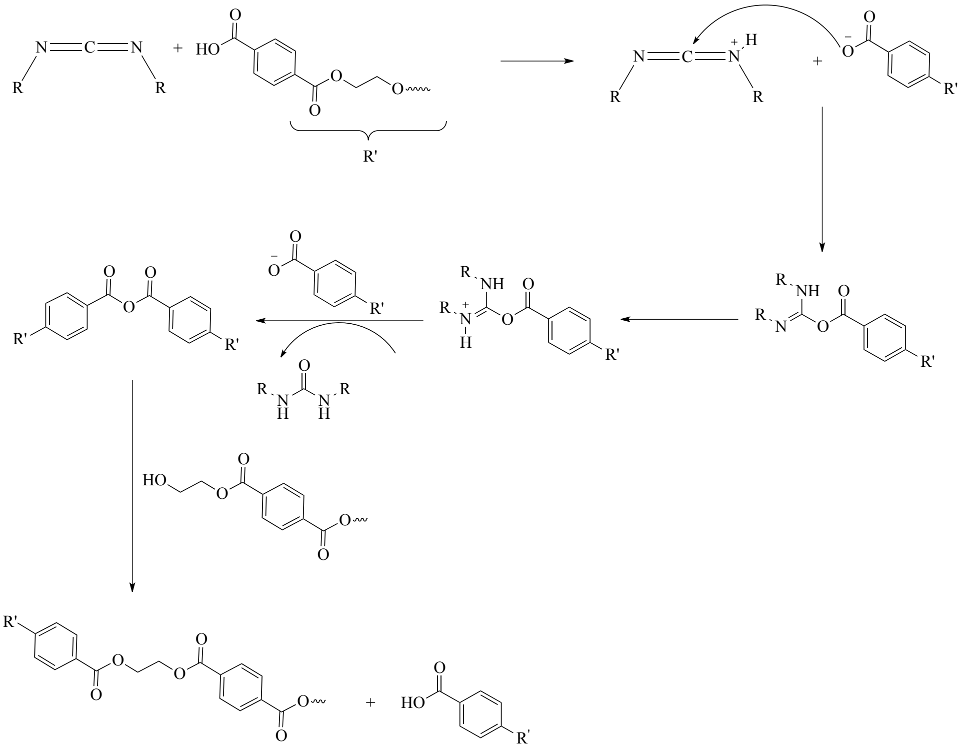

Figure 1.12. Reaction Mechanism of PET with Carbodiimide.

Diepoxides are reactive towards to COOH end groups. They form secondary alcohols. It is stated that these alcohols give reaction with COOH groups of PET chains and cause gelation and branching [22].

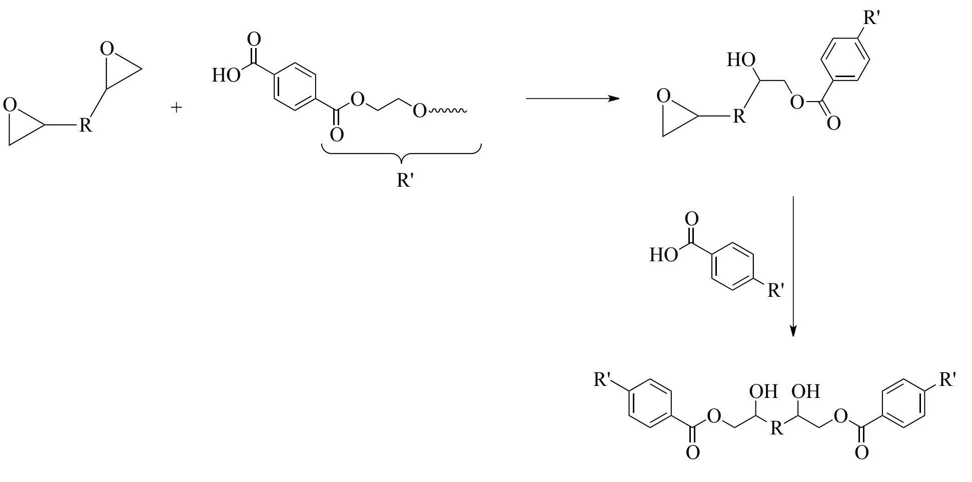

Figure 1.13. Reaction of PET with Diepoxide.

In the contrast to the other chain extenders mentioned and will be mentioned, dianhydrides are tetra-functional chain extenders. Therefore, they form branched and crosslinked PET. Dianhydrides are reactive towards -OH groups. PET chain extended with dianhydrides is suitable for applications where high melt strength is needed. As the branching percentage in the polymer network increases, melt strength of polymer increases [25].

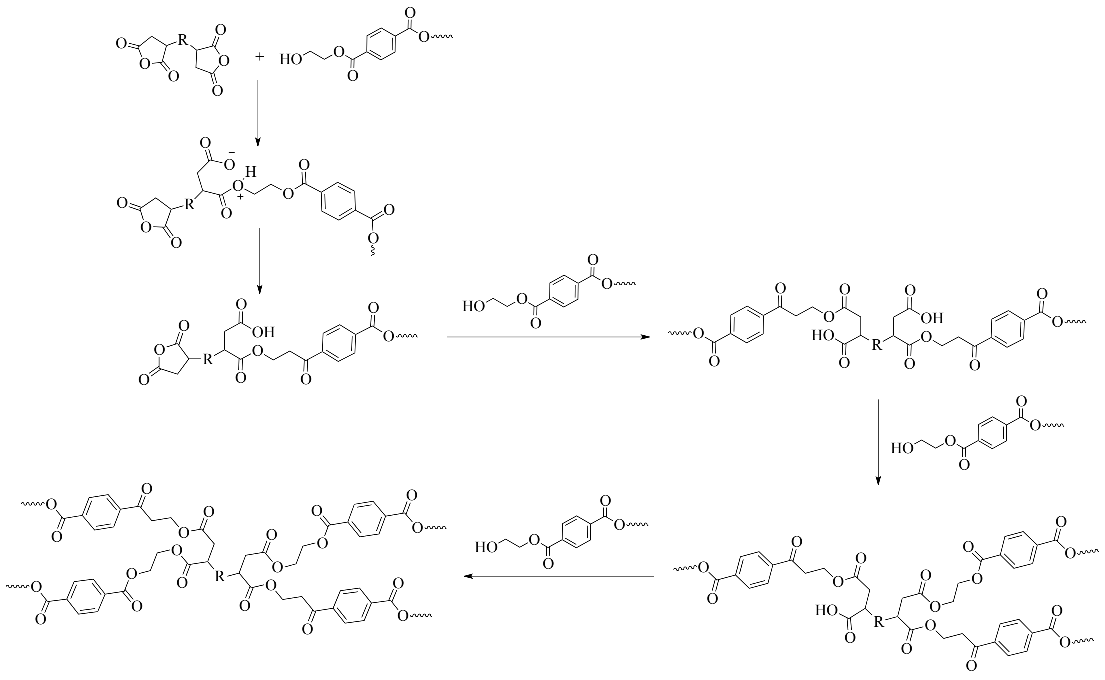

Figure 1.14. Reaction Mechanism of PET with Dianhydride.

Diisocyanates are both OH and COOH group reactive chain extenders. Reaction mechanisms are shown in Figure 1.15. Urethane linkages comprise in the backbone but the disadvantage of urethane linkages are their low thermal stability [22].

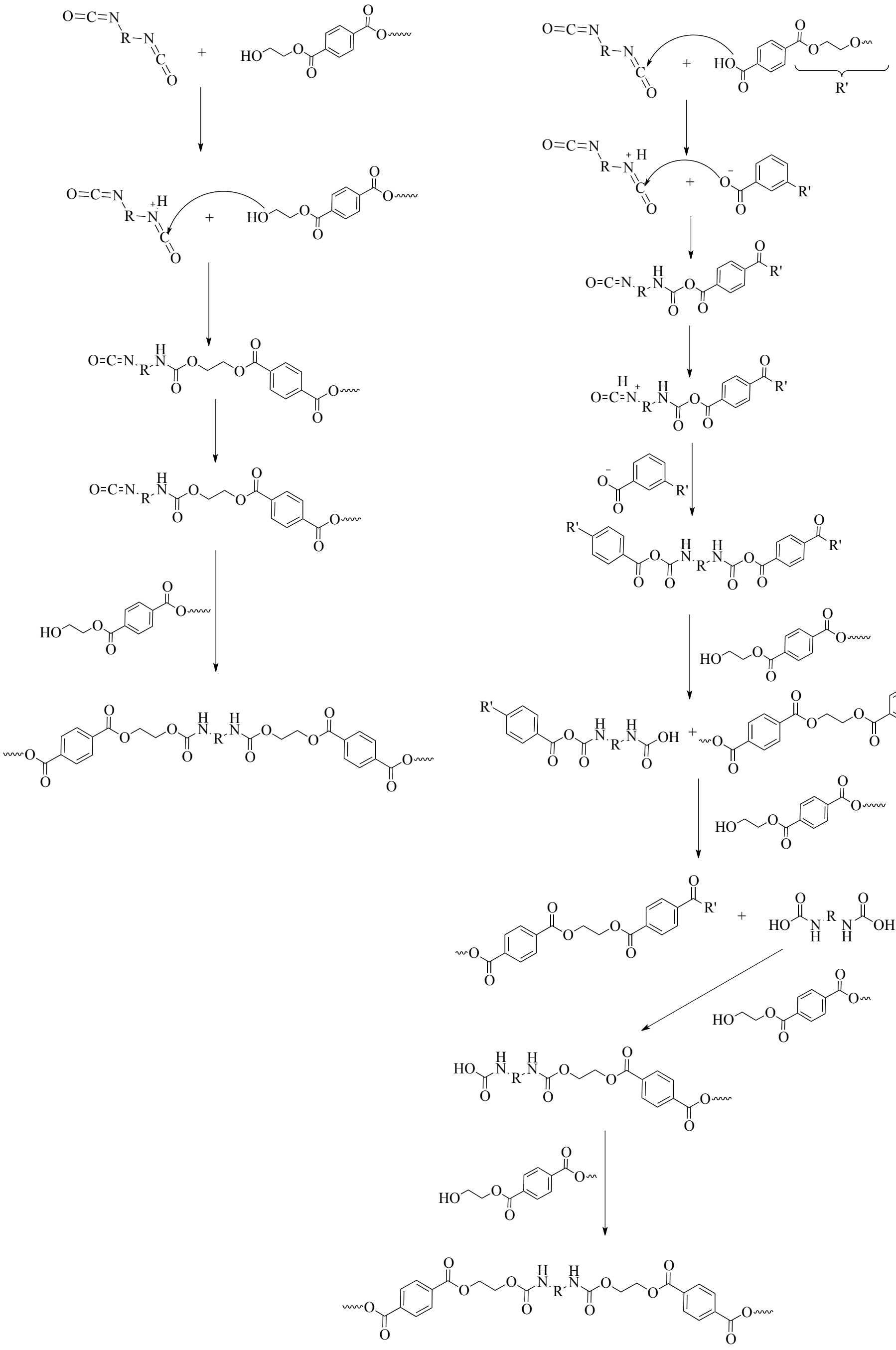

Figure 1.15. Reaction Mechanism of PET with Diisocyanate.

1.6.2. Methods For Chain Extension

Chain extension reactions are used to compensate the decrease in molecular weight of PET during production and processing.

Chain extenders can combine PET chains in a melt reactor, a SSP reactor or an extruder [31]. In a melt reactor, it is hard to control the viscosity of the new synthesized polymer. High cost of SSP is also a problem for chain extension reactions. However in an extruder these reactions may take place easily [25].

If the chain extension reactions occur in an extruder, the extrusion process is called “reactive extrusion”. PET is melted in an extruder with the help of heat and screw. Once PET melts homogeneously, chain extender is added to the extruder from a side feeder. Reactive extrusion method is faster than the other methods and it is easy to apply [25].

Even though it is easier to apply, there are lots of parameters to control in a reactive extrusion process. Temperature profile is the most important one and the profile chosen should be able to melt PET with minimum degradation. The other parameters are: chain extender type and amount, screw rate, throughput of molten PET and humidity of PET [25].

2. AIM OF THE STUDY

In the largest sense, the aim of this study is to put together the necessary experimental set ups and analytical approaches that will enable the laboratory scale screening of any novel or commercially available chain extenders which can be used in polyesters and/or polyamides. Thus, the methods employed should, in principle, allow to test any novel compound at the laboratory scale. In the present study such investigation was carried out by the example of PET. Commercially available and newly developed chain extenders were used to alter the molecular weight of PET. Amorphous PET was used as the starting material with four different chain extenders. Carbonyl biscaprolactam (CBC), 1,3-Phenylene-bis-oxazoline (PBO), DE and SO were used as chain extenders. Chain extension reactions were done in a melt polymerization set-up. The effects of chain extender type and chain extender amount were investigated with IV, CEG, GBC test results.

3. EXPERIMENTAL

3.1. Chain Extension Reactions of PET

Amorphous PET chips were used as starting material with four different chain extenders. Carbonyl biscaprolactam (CBC), 1,3-phenylene-bis-oxazoline (PBO), (DE) are commercially available. The fourth chain extender is SO synthesized by Sedef Özcan. PET chips were kept in the vacuum oven consistently and the chips that did not stayed at least 24 hours in the vacuum oven were not used in the experiments. The same conditions apply to the chain extenders. Experiments were done under nitrogen flow. Vacuum was only used for CBC- PET reactions.

Reactions were carried out in glass melt reactors and they were heated *via* ESM-4450 48 x 48 1/16 DIN Universal Input PID Process Controller with Smart I/O Module System and silicon oil was used for heat transfer to reactor. The reaction temperature was higher than the melting point of PET. Reaction time was set to 15 minute once the polymer started melting. Heidolph overhead stirrer was used. The rate of the stirrer was 50 rpm. Polymerization was followed *via* torque changes.

For each experiment, 15 g of ground PET was used. The amount of chain extenders used can be seen in Table 3.1.

Table 3.1. Stoichiometries of Reactions.

Mol of [COOH] or [OH] end group	CE type	CE mol (mmol)	Mol percentage of CE
1 [COOH]	PBO	1	20
1 [COOH]	PBO	2	33
1 [COOH]	PBO	3	43
1 [COOH]	PBO	4	50

Table 3.1. Stoichiometries of Reactions (contd.)

1 [COOH]	DE	1	20
1 [COOH]	DE	2	33
1 [COOH]	DE	3	43
1 [COOH]	DE	4	50
1 [OH]	CBC	1	20
1 [OH]	CBC	2	33
1 [OH]	CBC	3	43
[OH]	CBC	4	50
1 [OH]	SO	1	20
1 [OH]	SO	2	33
1 [OH]	SO	3	43
1 [OH]	SO	4	50

3.2. Gel permeation chromatography (GPC) Analysis

The samples were dissolved in hexafluoroisopropanol (HFIP) before GPC analysis.

3.3. Intrinsic Viscosity (IV) Analysis

The test method is confidential data.

3.4. Carboxyl End Group Analysis

The test method is confidential data.

4. RESULTS AND DISCUSSION

In this study, amorphous and four different chain extenders were used. All materials were dried in a vacuum oven prior to the experiments to prevent hydrolytic degradation. Melt polymerization set-up was used for chain extension reactions. Reactions were carried out at temperature higher than melting point of PET. Experiments were carried out under nitrogen to avoid thermooxidative degradation reactions. Vacuum was only used in experiments where CBC was employed to remove the caprolactam released upon deblocking of CBC since the latter process without vacuum resulted in polymers with air bubbles. Chain extension reactions were followed *via* torque change. At the beginning of the experiments (before melting) torque was around 15-16 N.m. When melting started, torque started to increase. It exceeded 25 N.m during reaction due to the IV increase.

To investigate the effect of chain extenders on PET, GPC, IV, CEG tests were performed.

As mentioned before, four different chain extenders were used in this study. Two of them, PBO and DE, are reactive towards carboxylic acid end groups. While the others, SO and CBC, are alcohol reactive chain extenders. As OH end group concentration is two to four fold higher than CEG concentration in PET, weight percentages of SO and CBC in reaction were higher than PBO and DE.

4.1. PBO and DE Effects on IV-CEG of PET.

PBO (Figure 4.1) is reactive at the sp^3 carbon bearing the oxygen on the oxazoline ring. The mechanism of reaction with PET is shown in Figure 4.2.

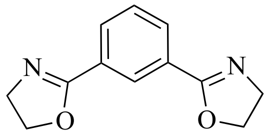

Figure 4.1. 1,3-Phenylene-bis-oxazoline.

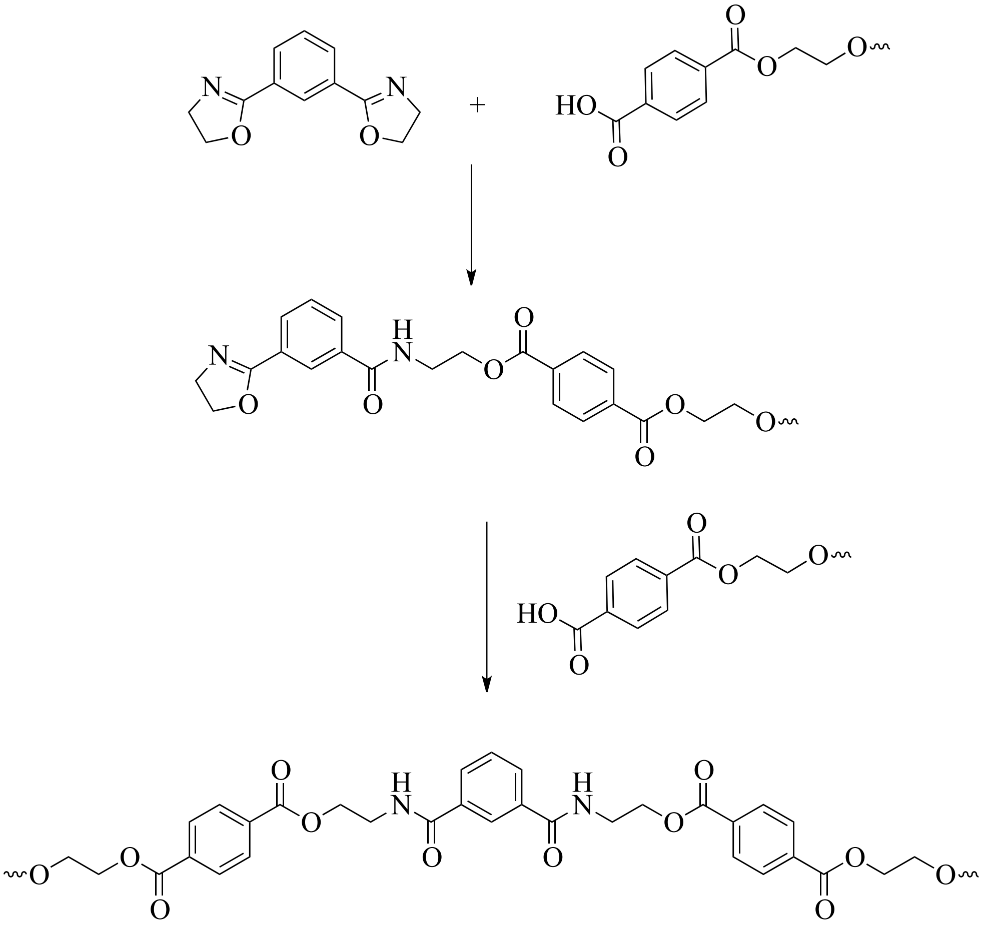

Figure 4.2. Reaction Mechanism of PET with 1,3-Phenylene-bis-oxazoline.

Structure of DE is in Figure 4.3. Reactivity of DE is more complicated than PBO. Theoretically, in acidic medium epoxy ring is opened from the most substituted carbon. Thus, at the end, primary alcohol formation is expected. However in polymeric systems, COOH end groups of PET attack the less substituted carbon of epoxy ring and form secondary alcohols according to the literature [8, 32, 33]. Reaction mechanism according to the literature can be seen in Figure 4.4.

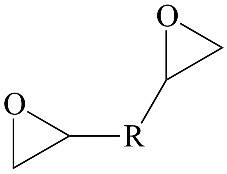

Figure 4.3. Diepoxide Structure.

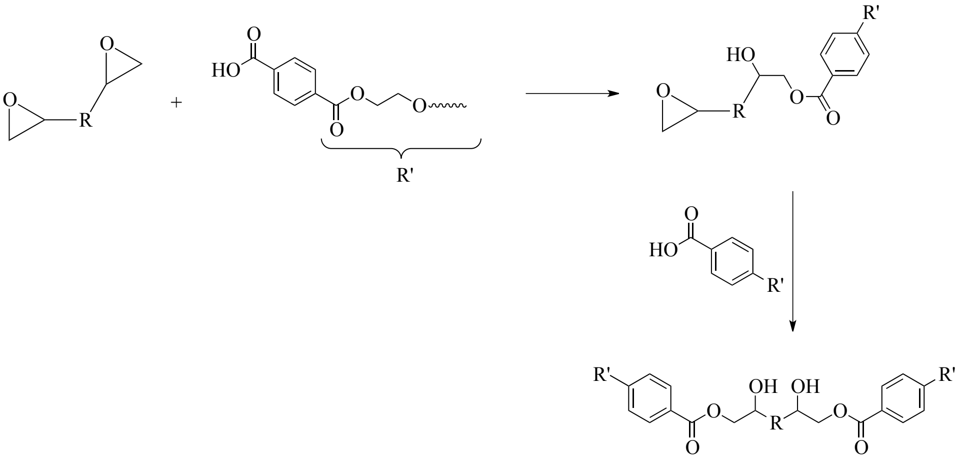

Figure 4.4. Reaction mechanism of PET with Diepoxide.

Through CEG test results, the amount of chain extender that was actually involved in reactions were calculated using the graph in Figure 4.5. According to this graph, neither CBC nor DE gave 100% yield. CEG results of DE are higher than both PBO and theoretical results.

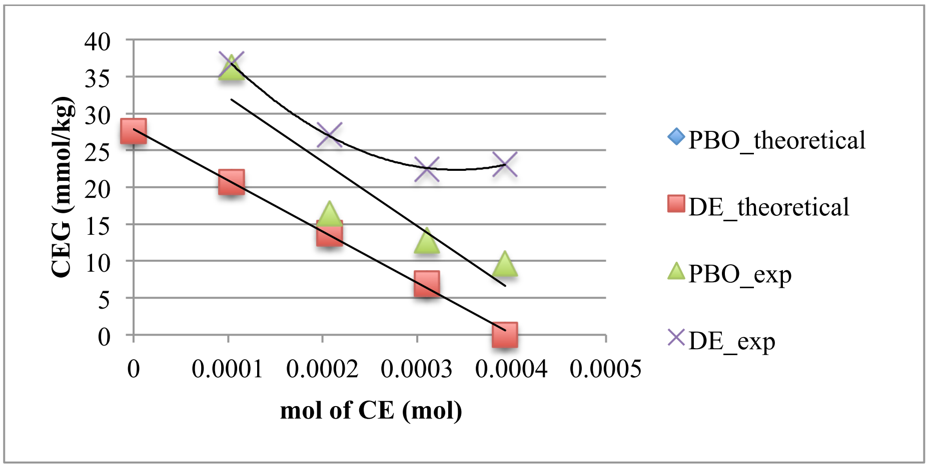

Figure 4.5. Carboxyl End Group Concentration *versus* Mol of Chain Extenders.

IV *versus* mol of CE and carboxyl end group concentration *versus* mol of CE.graphs were drawn according to data from Table 4.1 entries 2-4 and 5-7 for PBO and DE respectively.

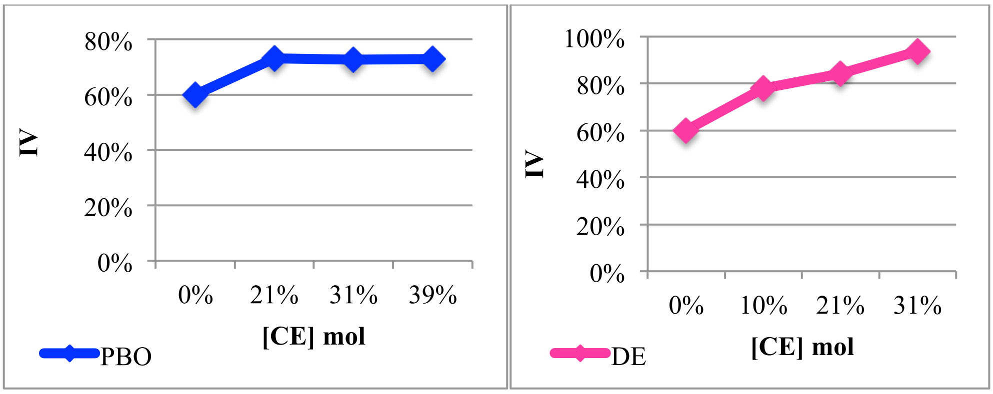

Figure 4.6. Intrinsic Viscosity *versus* Mol of CE.

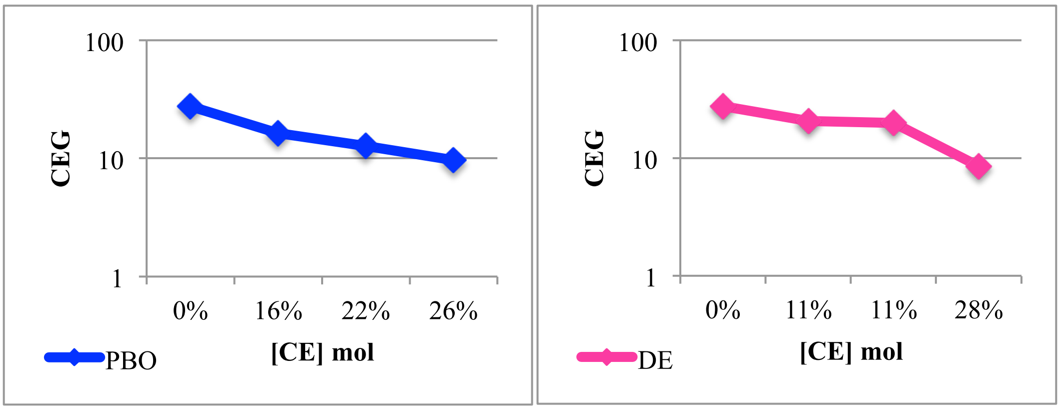

Figure 4.7. Carboxyl End Group Concentration *versus* Mol of CE.

According to the graph in Figure 4.6, PBO did not change IV of PET significantly. It is almost independent from PBO amount in the reaction. Whereas DE increased the IV more than PBO did. Accordingly as expected DE gave lower CEG concentration than PBO (Figure 4.7).

4.2. CBC and SO Effect on IV-CEG of PET

Structure of CBC can be seen in Figure 4.8. Carbonyl carbons of CBC are reactive towards OH end groups of PET as shown in Figure 4.9.

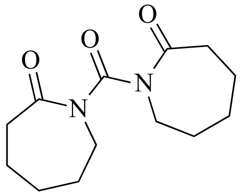

Figure 4.8. Carbonyl Biscaprolactam.

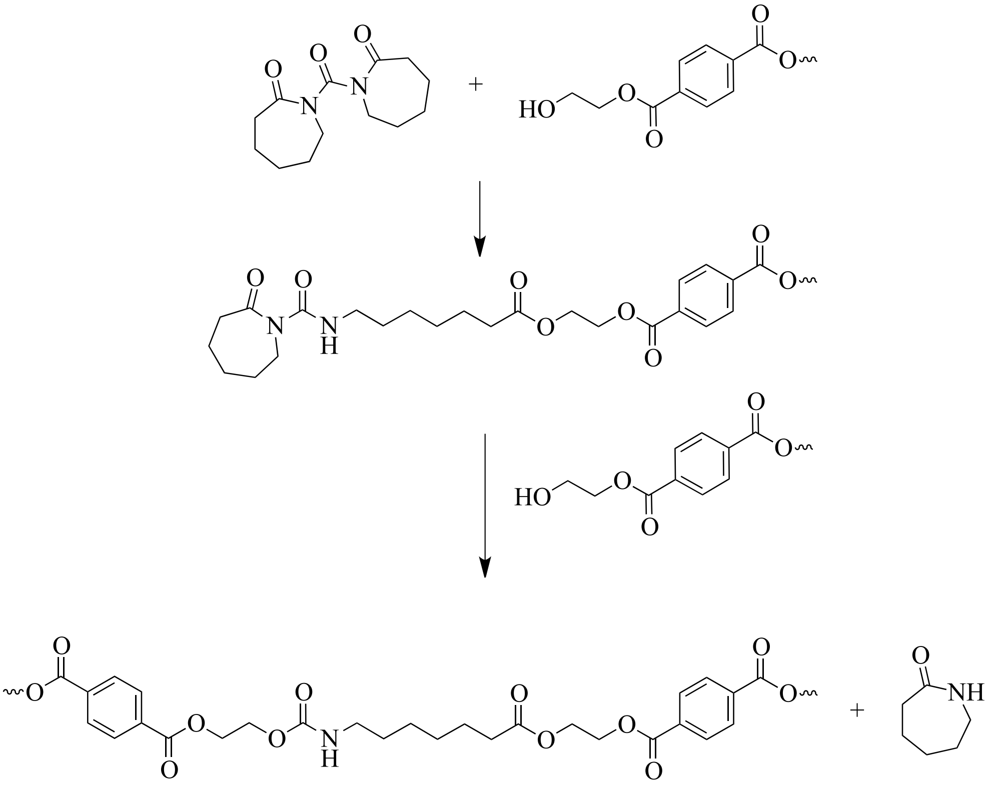

Figure 4.9. Reaction Mechanism of PET with Carbonyl Biscaprolactam.

SO is a new potential chain extender, which is reactive towards to OH end groups of PET. Its structure and reaction with PET is confidential data.

OH end group anaylsis could not be performed because there is no standard test procedure for the analysis. Therefore, the comparisons were done on the assumption that SO and CBC gave 100% yield.

IV *versus* mol of CE and carboxyl end group concentration *versus* mol of CE graphs were drawn according to data from Table 4.1 entries 8-10 and 11-13 for CBC and SO respectively.

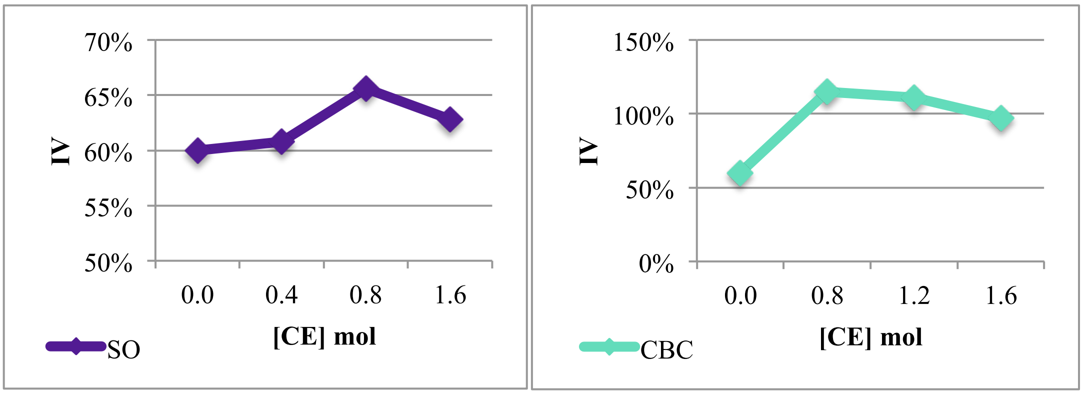

Figure 4.10. Intrinsic Viscosity *versus* Mol of CE.

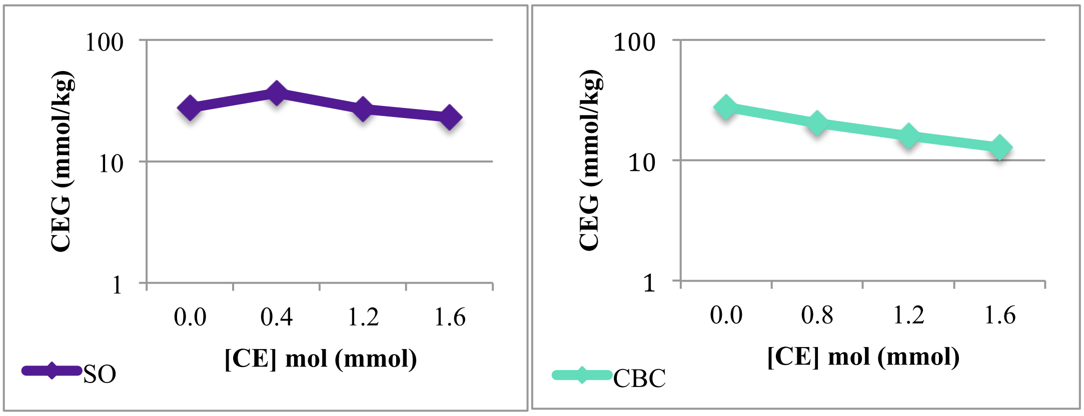

Figure 4.11. Carboxyl End Group Concentration *versus* Mol of CE.

According to graph in Figure 4.12. CBC increased the IV of PET more than SO did. It was not expected to see a decrease in CEG concentration since CE is theoretically not reactive towards COOH groups.. The reason of this decrease might be anhydride formation between two acid groups at high temperatures. The potential anhydride formation will be analyzed by GPC as a future work.

CEG *versus* IV graphs for all chain extenders were drawn according to Table 4.1.

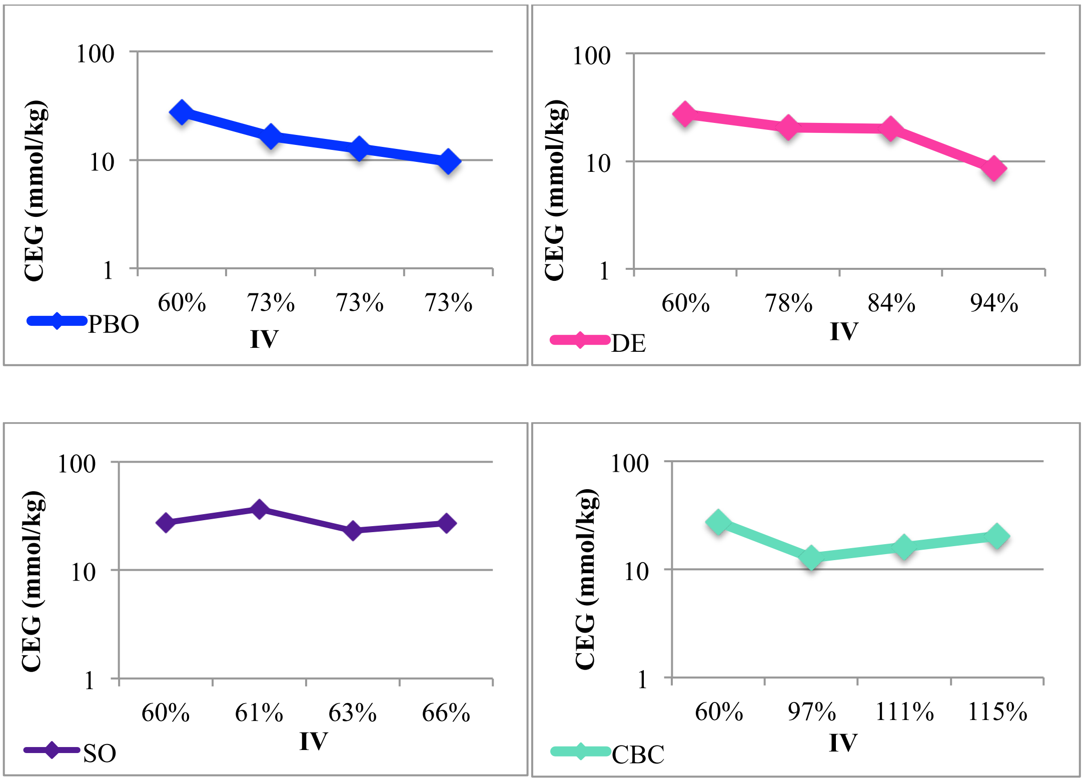

Figure 4.12. Carboxyl End Group Concentration *versus* Intrinsic Viscosity.

Chain extenders effects on IV and CEG were compared. The least effective one is SO according to Figure 4.14. It did not change the IV. Also, the highest CEG concentration was observed at SO chain extended PET. Whereas the lowest CEG concentration was observed with DE chain extended PET. However CBC chain extended PET gave the highest IV value. Generally IV and CEG are inversely proportional to each other. Thus the linear relationship of IV and CEG in CBC chain extended PET was unexpected and will be discussed next Section.

4.3. Chain Extenders Effect on Molecular Weight of PET.

GPC results gave us information about Mn, Mw and PDI values of the new chain extended PET. According to the results in Table 4.1, three types of graphs were drawn (Figure 4.15, Figure 4.16, Figure 4.17).

PDI is the unitless measure of the molecular weight distribution of a polymer, it is calculated from the ratio of Mw to Mn. It is expected to see inverse relationship between Mn and PDI from experimental results.

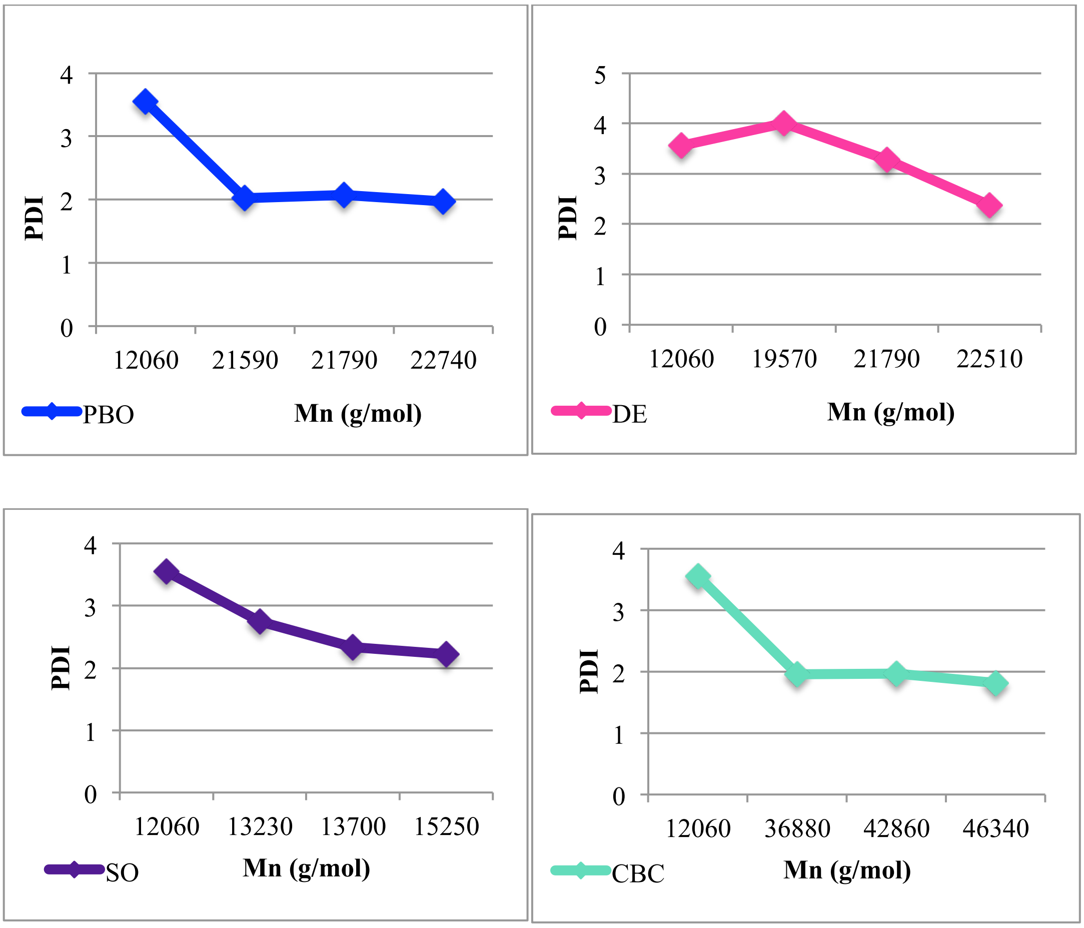

Figure 4.13. PDI *versus* Mn.

According to Figure 4.15 SO changed neither PDI nor Mn much. However PBO addition to PET decreased PDI value and increased Mn independent from the chain extender amount. DE chain extended PET gave the highest PDI value. The lowest PDI value was observed at CBC graph with highest Mn as expected. However PDI of CBC chain extended PET does not depend on the amount of CBC as can be seen Figure 4.15.

According to these results CBC chain extended PET is closer to monodispersity than the others whereas the highest increase in PDI was observed with DE. This result can be explained by the reaction mechanism differences between DE and CBC. CBC couples the OH end group chains but DE reacts with COOH end groups. Since the concentration of OH end groups is higher than the CEG concentration, CBC couples more chains. Therefore it decreases the PDI. Also this explains the hightest increase in Mw (Table 4.1 entries 8-10).

Mn depends on the number of chains in the polymer. As the CEG content increases, the number of chains increases and Mn decreases. It is expected to see reverse relation between CEG and Mn from Figure 4.16.

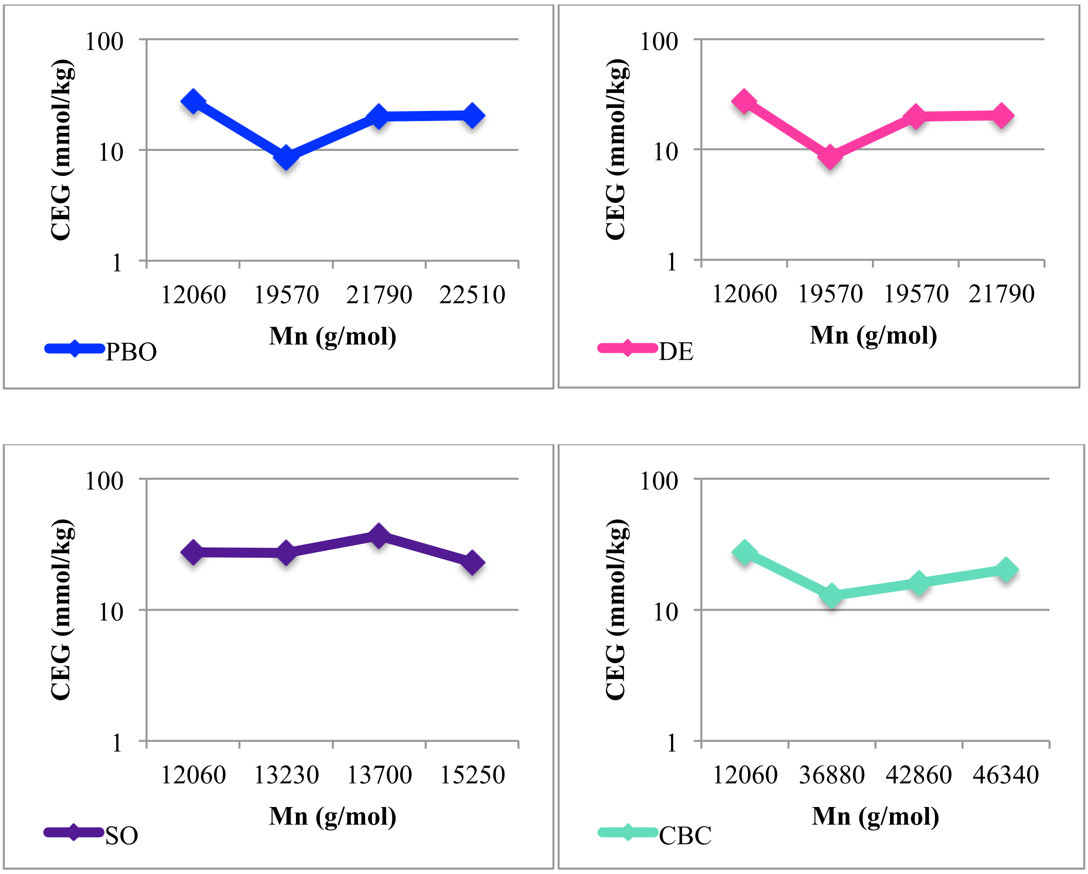

Figure 4.14. CEG *versus* Mn.

When new polymers CEG results are compared to initial PET with CEG=27,6 mmol/kg, (according to the Figure 4.16) chain extenders decreased the CEG and increased the Mn as expected. However as the Mn increased, CEG also increased which was an unexpected result. This result shows that CEG formation continues during chain extension reactions.

Mw depends on the size or weight of the polymer. IV depends on the molecular weight of the polymer. Therefore, it is expected to see a direct relationship between Mw and IV.

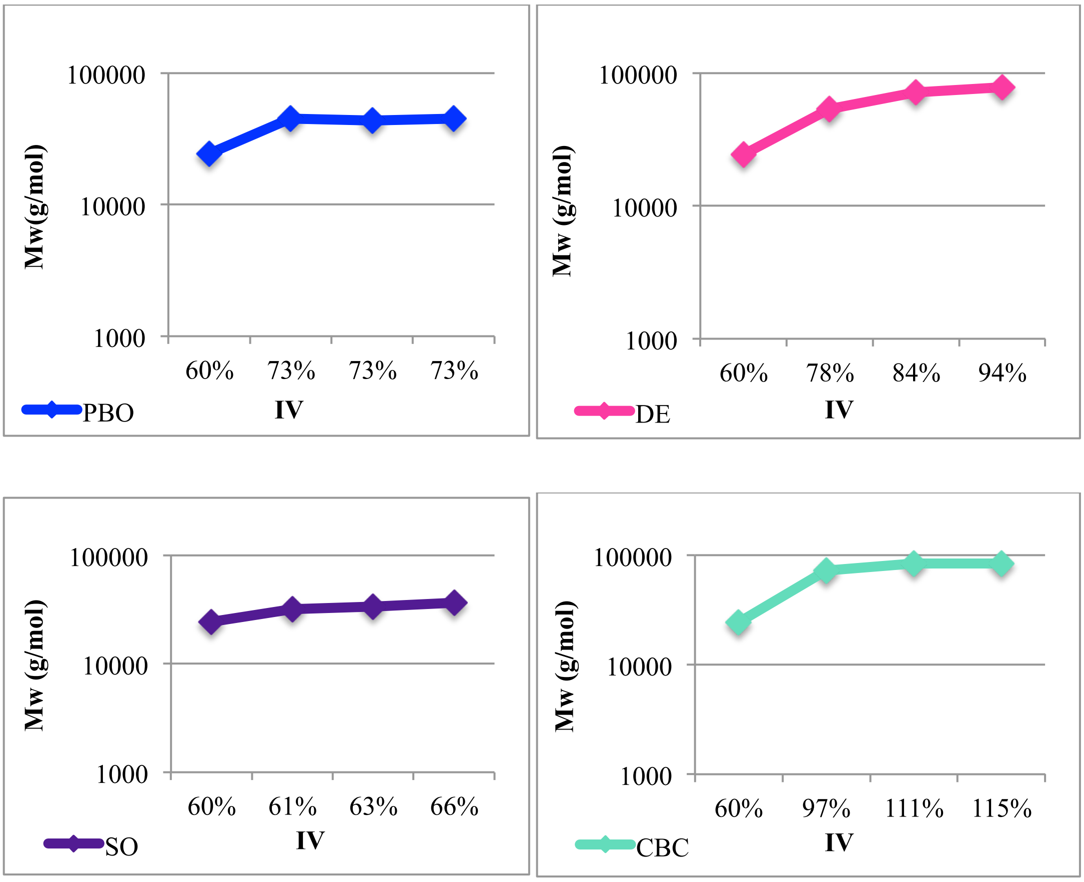

Figure 4.15. Mw *versus* IV.

According to Figure 4.17, the direct relation between IV and Mw is true. As the IV of the polymers increased, Mw of polymers also increased. The highest Mw increase with the highest IV was observed with CBC.

5. CONCLUSIONS

PET chains can degrade during both production and the processing steps. Molecular weight of PET decreases and CEG content increases during this degradation. To eliminate these problems chain extenders are used.

In this study, a lab scale screening of four different chain extenders was carried out by the example of PET. The effects of various chain extenders on PET were investigated. As a result all chain extenders increased the molecular weight and IV of PET. The most promising chain extender among the commercial ones is CBC which gave the highest increase in molecular weight. The novel synthesized chain extender, however, did not significantly increase the molecular weight.

6. FUTURE WORK

As a future work, the thermal characterization and mechanical strength of these chain extended polymers will be investigated. Also, OH end group analysis will be performed to have a complete knowledge about OH end group reactive chain extenders.

REFERENCES

1. Thomas S., P. M. Visakh, *Handbook of Engineering and Speciality Thermoplastics*, John Wiley & Sons, Vol. 3, Massachusetts, 2010.
2. Toufaili F. A. E., *Catalytic and Mechanistic Studies of Polyethylene Terephthalate Synthesis*, Ph. D. Thesis, Technical University of Berlin, 2006.
3. Eichhorn S. J., J.W.S. Hearle, M. Jaffe, T. Kikutani, *Handbook of Textile Fibre Structure*, Woodhead Publishing, Florida, 2009.
4. Fangueiro R., C. Gonilho Pereira, M. De Araújo, *Polyesters and Polyamides*, Woodhead Publishing,2008.
5. Awaja F., D. Pavel, "Recycling of PET", *European Polymer Journal*, Vol. 41, No. 7, pp. 1453–1477, 2005.
6. Venkatachalam S., S. Nayak, J. Labde, P. R. Gharal, K. Rao, A. K. Kelkar , "Degradation and Recyclability of Poly (Ethylene Terephthalate)," *Polyester*, pp. 75–98, 2012.
7. Shiraki S., Y. Tanaka, M. Sakai, "Process for The Preparation of Polyethylene Terephthalate", EP Patent, 0 389 948 B1, 1990.
8. Bikiaris D. N., G. P. Karayannidis, "Dynamic Thermomechanical and Tensile Properties of Chain-Extended Poly (ethylene terephthalate)", *Journal of Applied Polymer Science*, Vol. 70, pp. 797–803, 1998.
9. Ahmadnian F., *Kinetic and Catalytic Studies of Polyethylene Terephthalate Synthesis*, Ph. D. Thesis, Technical University of Berlin, 2008.
10. Dhavalikar R. R., *Reactive Melt Modification of Polyethylene Terephthalate*, Ph.D. Thesis, New Jersey Institute of Technology, 2003.
11. Bikiaris D. N., G. P. Karayannidis, "Thermomechanical analysis of chain-extended PET and PBT", *Journal of Applied Polymer Science*, Vol. 60, No. 1, pp. 55–61, 1996.

12. Awaja F., F. Daver, E. Kosior, F. Cser, “The Effect of Chain Extension on The Thermal Behaviour and Crystallinity of Reactive Extruded Recycled PET”, *Journal of Thermal Analysis and Calorimetry,* Vol. 78, No. 3, pp. 865–884, 2004.

13. Liu B., Q. Xu, “Effects of Bifunctional Chain Extender on the Crystallinity and Thermal Stability of PET”, *Journal of Materials Science and Chemical Engineering,* Vol. 1, 2013, pp. 9–15, 2013.

14. Ebewele,R. O., *Polymer Science and Technology*, CRC Press, Florida, 1996.

15. Ravindranath K., R. A. Mashelkar, “Modeling of Poly(Ethylene Terephthalate) Reactors - I. A Semibatch Ester Interchange Reactor”, *Journal of Applied Polymer Science*, Vol. 26, No. 10, pp. 3179–3204, 1981.

16. Bonner G. R., “Direct Coupling of Melt Polymerization and Solid State Processing for PET”, US Patent, 2005/0056961 Al, 2005.

17. Kim T. Y., S. a. Jabarin, “Solid-state Polymerization of Poly (ethylene terephthalate). III. Thermal Stabilities in Terms of The Vinyl Ester End Group and Acetaldehyde”, *Journal of Applied Polymer Science*, Vol. 89, No. 1, pp. 228–237, 2003.

18. T. Loontjens, K. Pauwels, F. Derks, M. Neilen, C. k. Sham, M. Sern, “The Action of Chain Extenders in Nylon-6, PET, and Model Compounds”, *Journal of Applied Polymer Science*, Vol. 65, No. 9, pp. 1813–1819, 1997.

19. Inata H., S. Matsumura, “Chain Extenders for Polyesters. III. Addition- Type Nitrogen-Containing Chain Extenders Reactive with Hydroxyl End Groups of Polyesters”, *Journal of Applied Polymer Science*, Vol. 32, pp. 4581-4594, 1986.

20. Kim T. Y., S. A. Jabarin, “Solid-State Polymerization of Poly (ethylene terephthalate). II. Modeling Study of the Reaction Kinetics and Properties”, *Polymer,* Vol. 89, pp. 228-237, 2003.

21. Japon S., L. Boogh, Y. Leterrier, J. a E. Manson, “Reactive processing of Poly(ethylene terephthalate) Modified with Multifunctional Epoxy-Based Additives”, *Polymer*, Vol. 41, No. 15, pp. 5809–5818, 2000.

22. Akkapeddi M. K., J. A. Gervasi, “Chain Extension of Polyethylene Terephthalate with Polyacyllactams”, US Patent, 4,857,603, 1989

23. Buxbaum L. H., “The Degradation of Poly (ethylene terephthalate)”, *Angew. Chem. internat. Edit*, Vol. 7, No. 3, pp. 182-190, 1968.

24. Dhavalikar R., M. Xanthos, “Parameters Affecting The Chain Extension and Branching of PET in The Melt State by Polyepoxides”, *Journal of Applied Polymer Science,* Vol. 87, No. 4, pp. 643-652, 2003.

25. Incarnato L., P. Scarfato, L. Di Maio, D. Acierno, “Structure and rheology recycled PET modified by reactive extrusion”, *Polymer*, Vol. 41, No. 18, pp. 6825-6831, 2000.

26. Agabekov V., V. Golubovich, S. Pesetskii, “Effect of Nanodisperse Carbon Fillers and Isocyanate Chain Extender on Structure and Properties of Poly(ethylene terephthalate)”, *Journal of Nanomaterials,* Vol. 2012, 2012.

27. Scheirs J., T. E. Long, “Additives for The Modification of Poly (ethylene terephthalate) to Produce Engineering-Grade Polymers”, *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters,* pp. 495-540, 2003.

28. Raffa P., M. B. Coltelli, S. Savi, S. Bianchi, and V. Castelvetro, “Chain Extension and Branching of Poly(ethylene terephthalate) (PET) with Di- and Multifunctional Epoxy or Isocyanate Additives: An Experimental and Modelling Study,” *Reactive and Functional Polymers*, Vol. 72, No. 1, pp. 50-60, 2012.

29. Nascimento, C. R., C. Azuma, R. Bretas, M. Farah, Marcos L. Dias1 J., “Chain Extension Reaction in Solid-State Polymerization of Recycled PET: The Influence of 2,20-Bis-2-oxazolineandPyromelliticAnhydride”, *Journal of Applied Polymer Science,* Vol.115, pp. 3177-3188, 2010.

30. Torres N., J. J. Robin, B. Boutevin, “Chemical Modification of Virgin and Recycled Poly(ethylene terephthalate) by Adding of Chain Extenders During Processing”, *Journal of Applied Polymer Science*, Vol. 79, No. 10, pp. 1816-1824, 2001.

31. Daver F., R. Gupta, E. Kosior, “Rheological Characterisation of Recycled Poly(ethylene terephthalate) Modified by Reactive Extrusion”, *Journal of Materials Processing Technology*, Vol. 204, No. 1–3, pp. 397-402, 2008.

32. Lacoste, J. F., V. Bounor-legaré, M. F. Llauro, C. Monnet, P. Cassagnau, A. Michel, “Functionalization of Poly (ethylene terephthalate) in the Melt State: Chemical and Rheological Aspects”, *Journal of Polymer Science*, Part A: Polymer Chemistry, Vol. 43, No. 11, pp. 2207-2223, 2005.

33. Marino X., M. W. Young, G. P. Karayannidis, and D. N. Bikiaris, “Reactive Modification of Polyethylene Terephthalate with Polyepoxides”, *Polymer Engineering and Science,* Vol. 41, No. 4, pp. 643-655, 2001.