ดีพอลิเมอไรเซชันของพอลิเอทิลีนเทเรฟทาเลตโดยตัวเร่งปฏิกิริยาคอปเปอร์(II)คลอไรด์ไดบิวทิลทินออกไซด์และซิงค์แอซีเทตในเครื่องปฏิกรณ์แบบแบตซ์

นางสาวนฤภัทร ตั้งมั่นคงวรกูล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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DEPOLYMERIZATION OF POLY(ETHYLENE TEREPHTHALATE) BY COPPER(II)CHLORIDE, DIBUTYLTIN OXIDE AND ZINC ACETATE CATALYSTS IN BATCH REACTOR

Miss Naruephat Tangmankongworakoon

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จุดประสงค์ของงานวิจัยนี้คือ การนำเอาพอลิเอทิลีนเทเรฟทาเลตที่ใช้แล้วซึ่งจัดว่าเป็นของเสียที่มีเป็นจำนวนมากในประเทศไทยโดยนำกลับมาเป็นสารตั้งต้นคือ ไดเมทิลเทเรฟทาเลต ซึ่งใช้ปฏิกิริยาดีพอลิเมอไรเซชันของพอลิเอทิลีนเทเรฟทาเลตกระทำในเครื่องปฏิกรณ์แบบแบตช์ซึ่งบรรจุสารละลายของพอลิเอทิลีนเทเรฟทาเลตในเมทานอลโดยใช้ คอปเปอร์(II)คลอไรด์ไดบิวทิลทินออกไซด์และซิงค์แอซีเทต เป็นตัวเร่งปฏิกิริยา จากการทดลองพบว่าไดบิวทิลทินออกไซด์เป็นตัวเร่งปฏิกิริยาที่ว่องไวมากที่สุดต่อปฏิกิริยาดีพอลิเมอไรเซชันของพอลิเอทิลีนเทเรฟทาเลตที่อุณหภูมิ 160-190 °C เวลาในการทำปฏิกิริยา 5-40 นาที และอัตราส่วนโดยน้ำหนักของตัวเร่งปฏิกิริยาต่อพอลิเอทิลีนเทเรฟทาเลต 0.3-2% จากผลการทดลองพบว่า ภาวะที่เหมาะสมของปฏิกิริยาดีพอลิเมอไรเซชันของพอลิเอทิลีนเทเรฟทาเลตโดยไดบิวทิลทินออกไซด์เป็นตัวเร่งปฏิกิริยาคืออุณหภูมิ 170-180 °C เวลาในการทำปฏิกิริยา 20-25 นาที และ อัตราส่วนโดยน้ำหนักของตัวเร่งปฏิกิริยาต่อพอลิเอทิลีนเทเรฟทาเลต 0.8% ให้ร้อยละผลได้ของสารผลิตภัณฑ์ร้อยละ 97 นอกจากนี้งานวิจัยนี้ได้ศึกษาแบบจำลองจลนพลศาสตร์ของปฏิกิริยาดีพอลิเมอไรเซชันของพอลิเอทิลีนเทเรฟทาเลตโดยใช้ไดบิวทิลทินออกไซด์เป็นตัวเร่งปฏิกิริยาเป็นปฏิกิริยาอันดับหนึ่ง และได้ค่าพลังงานกระตุ้น 154.05 กิโลจูลต่อโมล

ภาควิชา........เคมีเทคนิค............. ลายมือชื่อนิสิต...
สาขาวิชา.......เคมีเทคนิค..............ลายมือชื่ออาจารย์ที่ปรึกษา.......................................
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NARUEPHAT TANGMANKONGWORAKOON : THESIS TITLE DEPOLYMERIZATION OF POLY(ETHYLENE TEREPHTHALATE) BY COPPER(II)CHLORIDE, DIBUTYLTIN OXIDE AND ZINC ACETATE CATALYSTS IN BATCH REACTOR THESIS ADVISOR : PROF. SOMSAK DAMRONGLERD, Dr.Ing., THESIS COADVISOR : ASSOC. PROF. THARAPONG VITIDSANT, Dr.de l'INPT., 100 pp. ISBN 974-53-1435 -8.

The objective of this study is to converse the used Polyethylene terephthalate classified as a great deal of waste available in Thailand to its original reactant(Dimethyl terephthalate). Regarding the procedure, the depolymerization process was performed in a cylindrical reactor capacity 70 ml. which was constructed with stainless steel 316. PET was dissolved in methanol solution and mixed with these catalysts. The reaction was operated in temperature range 160 ^{o}C-190 ^{o}C, reaction time in the range of 5 min-40 min. and ratio of catalyst-to-PET in the range of 0.3%-2.0% by weight.

The experimental result indicated that the optimal condition of the depolymerization of PET with dibutyltin oxide as a catalyst was at the temperature ranging from 170 ^{0}C to 180 ^{0}C, the reaction time of 20 min to 25 min and the catalyst-to-PET ratio of 0.8 %. The yield percentage of the product(DMT) was 97. In addition, this research had also studied the model of kinetic depolymerization of PET using dibutyltin oxide as a catalyst. The result showed that it was a first-order reaction with the activation energy of 154.05 KJ/mol.

Department........Chemical Technology............Student’signature...................................
Field of study.....Chemical Technology............Advisor’s signature............................
Academic year 2004 Co-advisor’s signature...................................

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CHAPTER I

INTRODUCTION

1.1 INTRODUCTION

Poly(ethylene terephthalate) (PET)[1] is widely in used manufacturing everyday life consumer product especially the containers such as bottles for drinks, high strength of fibers and photographic films. All of for bottles and containers there product do not friendly produce hazard to the environment, and created many problems. The treatment of plastic wastes [2] has become a major environmental problem. It can be disposed in landfill sites or burning or recycle. Landfill is becoming much more expensive and undesired system for many cities. The destruction of wastes by incineration is prevalent, but this practice is expensive and if we face the problem with unacceptable emissions. The appropriate choice alternative would be recycling. Recycling is economic safe treating this and energy from wastes.

The recycling of waste plastic products by catalytic cracking has some advantages over thermal degradation (noncatalytic method). An adequate catalyst in catalytic cracking process will give the proper reaction conditions and it will have a great potential to receive, or narrow the product distribution. Thus, a catalytic cracking process could be a more efficient and economical way to recycle waste PET products than the noncatalytic process.

In this study, the series of experiments will be conducted by the process of depolymerization of PET with three catalyst, particularly to study the effects of the temperature, reaction time and catalyst-to-PET weight ratio. PET can be depolymerized to dimethyl terephthalate, ethylene glycol and oligomers. It can be shown by the figure 1.1

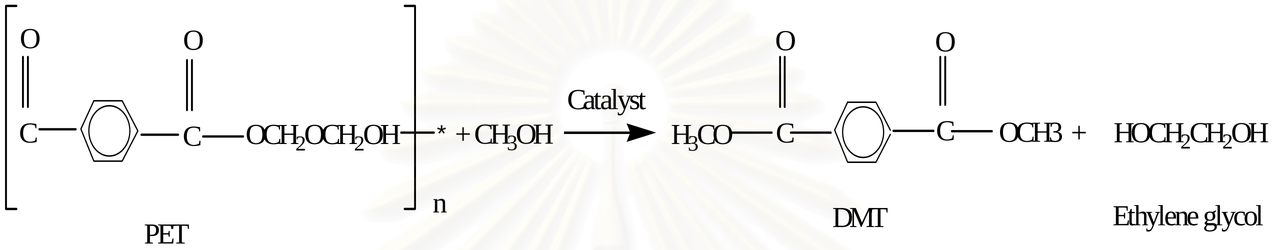


Figure 1.1 The mechanism of depolymerization of PET in batch reactor.[3]

1.2 The objectives of this study are :

1. To study the Depolymerization of Polyethylene terephthalate processed with three catalyst; Cu(II)chloride Dibutyltin oxide and Zinc acetate.
2. To investigate the effect of parameters such as concentration of the catalyst, temperature and reaction time
3. To identify the pathway of the reaction and develop a kinetic model for depolymerization of polyethylene terephthalate process.

CHAPTER II

LITERATURE REVIEW

Theory

Chemical recycling of PET including methanolysis, hydrolysis, glycolysis, aminolysis, and degradation or cracking provides a way to recover raw materials, such as terephthalic acid and ethylene glycol or oligomer, and some other useful small molecules. Chemical recycling of wasted PET products will thus be a more resourceful and valuable way[4-9].

Treatment of waste plastic products by catalytic cracking has some advantages over thermal degradation (noncatalytic method). Applying an adequate catalyst in catalytic cracking process at proper reaction conditions has a great potential to lower the required cracking temperature, shorten the cracking time, increase the cracking ability of plastics, and narrow the product distribution. Thus a catalytic cracking process could be a more efficient and economical way to recycle waste PET products than the noncatalytic process.

2.1 PET preparation [1]

PET is a kind of polymer that synthesize from the polymerization reaction between ethylene glycol and dimethyl terephthalate(in the ester exchange type) as the figure 2.1-2.2

It can be explained into 2 steps:

Step I Initially, dimethyl terephthalate and ethylene glycol were mixed together in the ratio of 2.1 – 2.2 . In addition a catalyst used might have been PbO. However carbonate, oxide, alkanoates and alkoxide of metal (such as Ba, Cd, Co) are used more widely. The initial temperature in the range of 150 to 210 ^{o}C. The ester exchange that occurred in step 1 following;

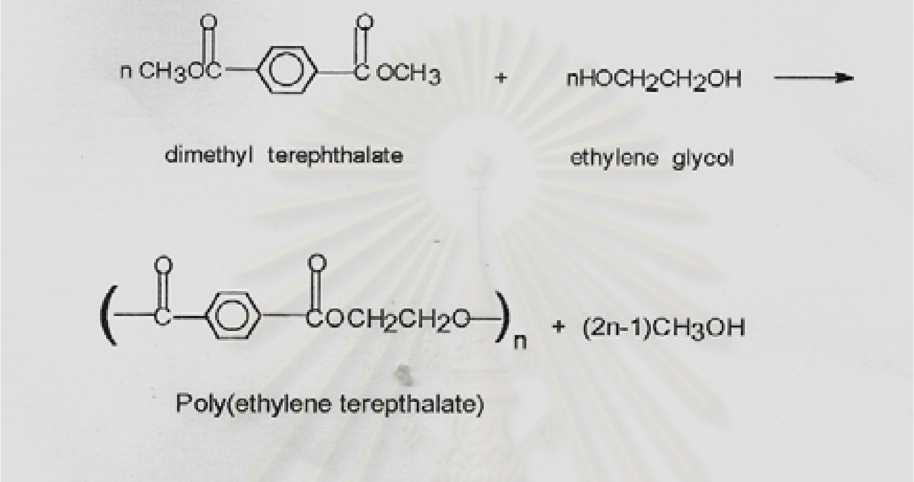
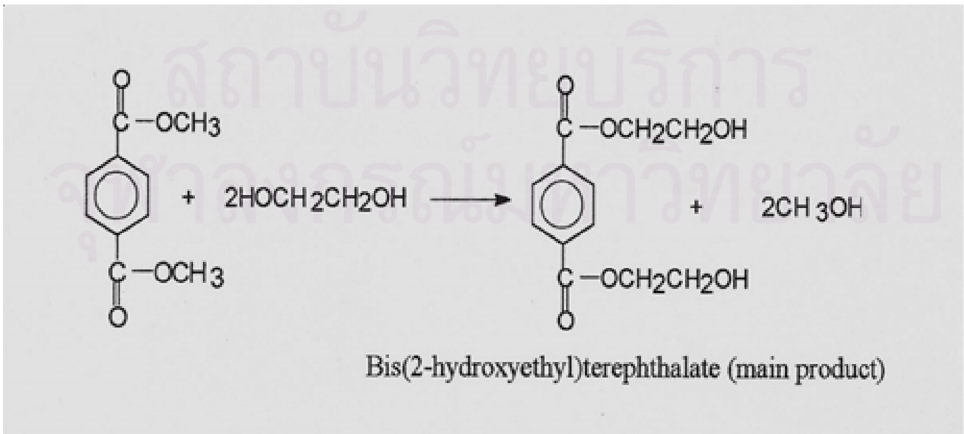


Figure 2.1 The mechanism of polymerization of PET .



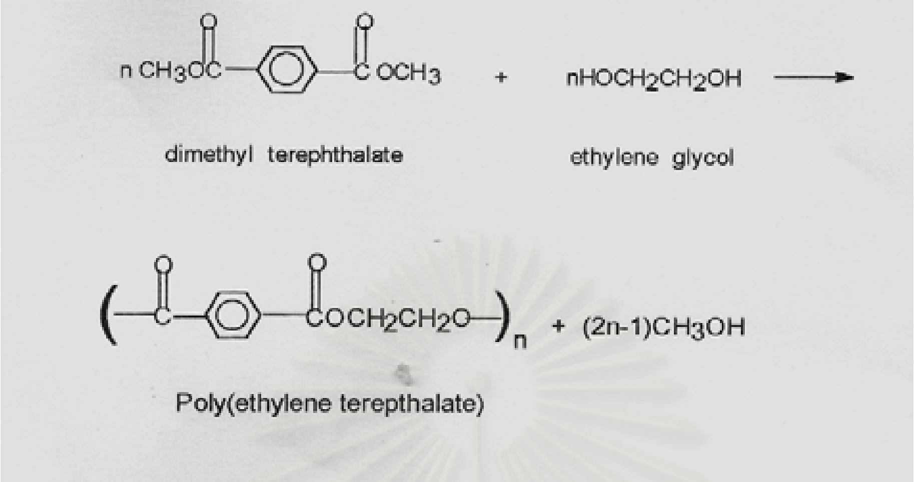


Figure 2.1 (continue) The mechanism of polymerization of PET .

The main product of this reaction was bis(2-hydroxyethyl)terephthalate. Other product was oligomer. In addition, a byproduct could have supported to change the equilibrium of the reaction continuously. This process could have supported to change the equilibrium of the ester exchange reaction to the right side of the chemical reaction. Step II Products from step I was heated until the temperature was increased to the range of 270 ^{o}C to 285 ^{o}C. Meanwhile, Pressure was decreased until it was below 1 mmHg by pumping. Bis(2-hydroxylethyl)terephthalate was condensed under this condition(high temperature, low pressure). Ethylene glycol was separated from this reaction continuously. Generally the molecular weight of PET was approximately 20,000. PET was extruded from reactor while it was melted. Finally, PET was transformed by spinning into fiber or melting into film.

2.2 **Factor affecting polymer stability** [11-20]

The chemical structure of the polymer is of primary importance in respect to its stability. The chemical composition (i.e., what kinds of chemical bonds in what sort of arrangement) is in itself a decisive factor. Bond energies between the same atoms are very different depending on the chemical groups to which the atoms belong. A few selected data are included in Table 1

Tertiary and allylic bonds are usually weaker than primary or secondary ones. In polymers consisting only of primary and secondary carbon atoms (e.g., PVC), the present of such bonds is undesirable because these form weak sites which are very easy to attack. Processess leading to these bonds during polymerization (e.g., PVC branching or dehydrochlorination) are to be avoided. The dissociation energies of the various bonds in the polymer may determine the course of degradation: the process always begins with the scission of the weakest available bond or with an attack at this site; and the first step usually determines the further direction of the process. Other components of the chemical structure, such as steric factors, stability of the intermediates, or the possibility of their resonance stabilization, may also have great influence on degradation. Such factors may even change the value of the bond dissociation energies.

Table 1 Bond Dissociation Energies of Various Single Bonds.

Bond broken A-B	Bond Dissociation energies (KCAL/MOL)	Bond broken A-B	Bond Dissociation energies (KCAL/MOL)
C_2H_5-H	99	C_6H_5-CH_3	94
n-C_3H_7-H	98	$C_6H_5CH_2$-CH_3	72
t-C_4H_9-H	91	CH_3-Cl	84
CH_2=$CHCH_2$-H	82	C_2H_5-Cl	81
C_6H_5-H	103	CH_2=$CHCH_2$-Cl	65
$C_6H_5CH_2$-H	83	CH_3-F	108
C_2H_5-CH_3	83	C_2H_5-F	106
n-C_3H_7-CH_3	83	HO-OH	51
t-C_4H_9-CH_3	81	t-C_4H_9O-OH	36

The tacticity of the polymer plays an important role in the degradation behavior. Atactic and isotactic polypropylene have very different oxidative stability (the isotactic one is much more stable). Syndiotactic PVC prepared at low temperature has increased stability compared to the ordinary material produced at about 50 °C. It is, however, very difficult to separate the effect of tacticity is usually connected with a change of morphology.

Physical and morphological factors may also influence polymer stability. It is well known that oxidation is always initiated in the amorphous phase of semicrystalline polymer and the propagation of the oxidation into the crystalline phase is a result of the destruction of the crystalline order. Thus, crystallinity is an important characteristic of the polymer from the viewpoint of stability

The morphology of the material is usually more stable against oxidation because the diffusion of oxygen into the product is more difficult than with a material of loose structure. On the other hand, the facile diffusion of HCl evolved from PVC with a loose morphology reduces the autocatalytic character of the degradation which may lead to a catastrophic destruction on the case of compact and dense materials.

Similar to the internal chemical stresses already mentioned (weak sites,etc.), the internal mechanical stresses may or introduced by finishing operations are very dangerous. Such stresses may serve not only as sources of later mechanical deterioration but also as initiators of, or assistants to, various chemical attacks. This is especially true in cases of stresses with long duration (the so-called stress corrosion of polymers).

The role of contaminants is quite obvious and has already been mentioned in connection with the synthesis of polymers. It is obvious that some additives intentionally present in the material, such as plasticizers or lubricants, influence the stability of the composite, especially if the oxidizability and biodegradability of such systems are higher than those of the polymer components. Once radicals are formed in the additive, they attack the polymer and vice versa; i.e., composites are sometimes less stable than their components. In special cases, additives are intentionally used to promote degradation of the composites (e.g., photosensitizers or plasticizers) which are specific culture media for bacteria in some rural and horticultural applications. On the other hand, additives may stabilize the polymer; the use of antioxidants, photostabilizers, etc., which we discuss later in detail, is based on this fact

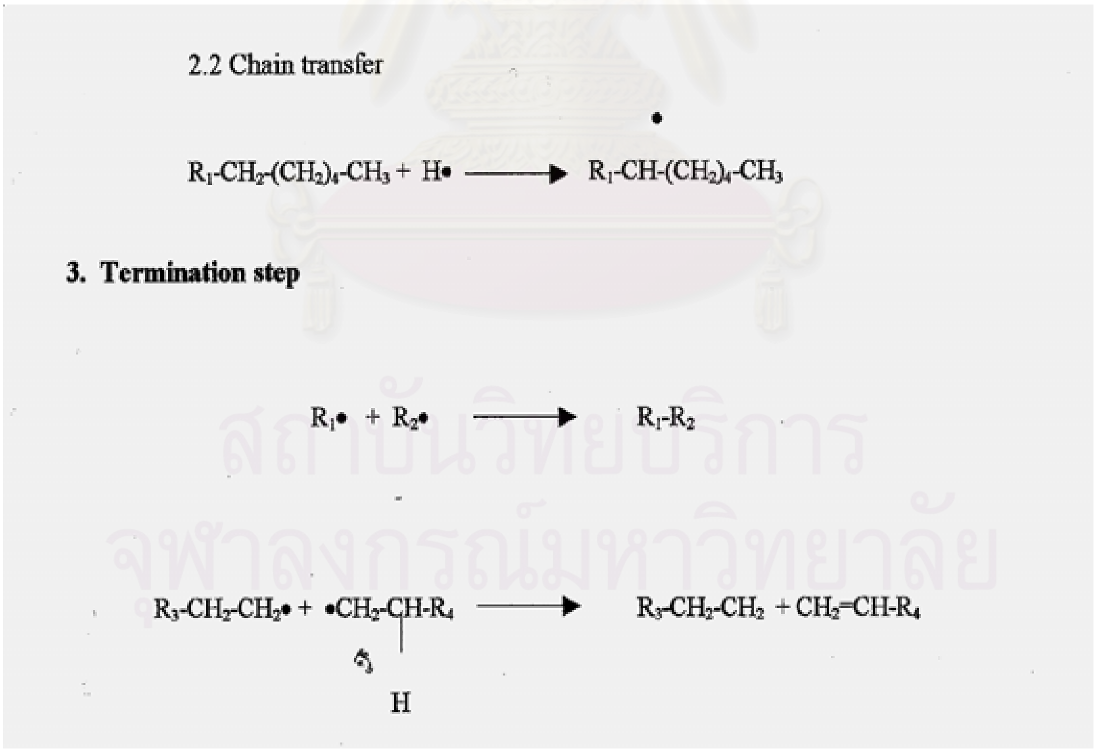
2.3. **The mechanism of depolymerization of PET** [21-23]

Depolymerization is the inverse of polymerization, namely, a stepwise separation of the monomers from the growing chain end. By the depolymerization reaction may happen as the process following;

2.3.1 Thermal cracking process.

Thermal cracking, where free radicals (lacking one hydrogen atom on carbon atom in the hydrocarbon molecule) are intermediate species which cracked by a ß-scission mechanism. The most successful present explanation of thermal cracking of hydrocarbon is Rice free radical theory as modified by Kossiakoff and Rick. This will be called the “RK-theory as follows to explain the cracking of normal paraffin: The normal paraffin molecule loses a hydrogen atom by collision and reaction with a small free hydrocarbon radical or a free hydrogen atom, thereby becoming a free radical itself. This radical may immediately crack or may undergo radical isomerization prior cracking. Radical isomerization presumably occurs through a coiled configuration of a single radical, in which the hydrogen donor and acceptor carbon atom much closely approach each other. Radical isomerization is a change of the position of hydrogen atom, usually to yield a more stable radical in order of tertiary>secondary>primary free radical.

Cracking of either the original or isomerized radical then takes place at a C-C bond located in the β position to the carbon atom lacking one hydrogen atom. Cracking at the β position gives directly an α-olefin and a primary radical (lacking one hydrogen atom on primary carbon atom); in this step no change of position any hydrogen atom with respect to the carbon skeleton. The primary radical derived from this step may immediately recrack at the β bond to give ethylene and another primary radical, or it may first isomerize. In the absence of radical isomerization, only primary radicals are derived from cracking reaction of normal paraffin; primary radicals thus give only ethylene as the olefin product. Radical isomerization reduces the amount of ethylene, but it still remains the major product. By successive cracking, the radicals then react with feed stock molecules to produce new free radicals and are themselves converted to methane or ethane. Thus, cracking is propagated as chain reaction. A schematic representation of linear paraffin cracking is as follows;



2.3.2 Depolymerization of PET[24-26]

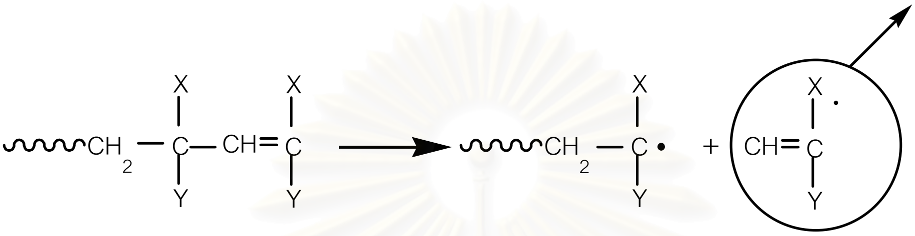
Depolymerization is essentially a reversal of the polymerization process. In the simplest case, depolymerization consists of initiation at chain ends, depropagation, and termination. In the depropagation step, monomer is unzipped rapidly from the activated chain ends. The main characteristic of degradation processes with dominating depolymerization character is the high monomer yield.

Depolymerization is not the only way in which a polymer can undergo degradation. The type of degradation favored under the given circumstances is the fastest among the possible reactions. Thus, polymethyl methacrylate(PMMA) can depolymerize (~250 ^{o}C), undergo random chain scission (~300 ^{o}C), and lose methanol (~320 ^{o}C). However, we classify PMMA as a depolymerizing material because depolymerization is that degradation process which takes place at the lowest temperature when the temperature is raised continuously as in thermogravitymetry.

2.3.3 Chemical and Thermodynamic aspects of Depolymerization

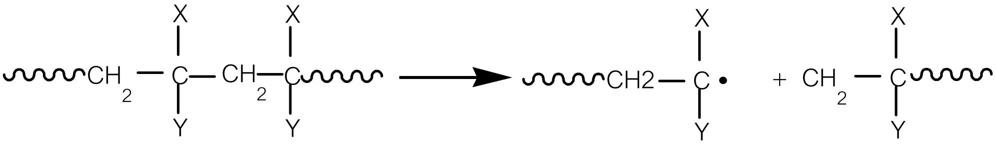
Depolymerization can be the dominating degradation process of a polymer if (A) initiation by main chain scission is possible, (B) the intermediates of the process are stable, and (C) the unzipping of monomers requires a relatively small activation energy.

(A) Initiation by main chain scission is a necessary condition of depolymerization because this process produces the terminal active site capable of depropagation. Although depolymerization can be initiated by random chain scission or by scission at the weak sites built into the main chain, initiation at the chain end is typical. This is usually possible if the chain end itself is a weak site of the polymer as in the case of macromolecules with terminal double bond formed by termination with disproportion of the growing radicals:



(2.3-1)

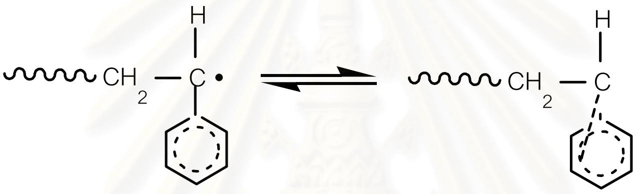
The monomer radical formed in this reaction usually volatilizes, but the macroradical remains in the systems as long as its length is higher than the volatilization limit at the degradation temperature, which is generally small as compared to the length of macromolecules. Both X and Y in reaction (2.3-1) may be hydrogen , but disubstituted polymers(because of the stability requirement) undergo more facile depolymerization. In initiation by random chain scission, two macroradicals are formed with different terminal groups. Thus the possibility of side reactions distorting the depolymerization character of the process is higher than with chain-end initiation:



(2.3-2)

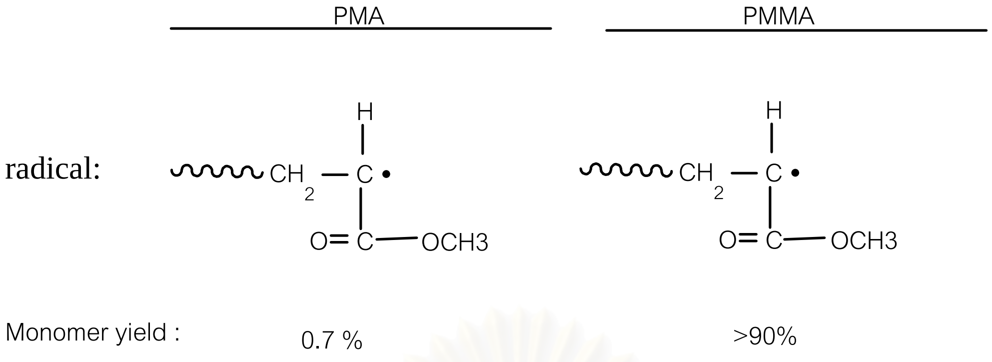
The amount of polymer molecules with terminal double bonds and the possibility of chain-end initiation may be decreased by various methods, including the addition of chain transfer agents to the polymerization system.

(B) The terminal radicals formed in the initiation step or in the depropagation steps must be stable enough to not participate in various side reactions such as chain transfer. This condition can be fulfilled in various ways: The radical can be stabilized by resonance stabilization, as in polystyrene(PS):



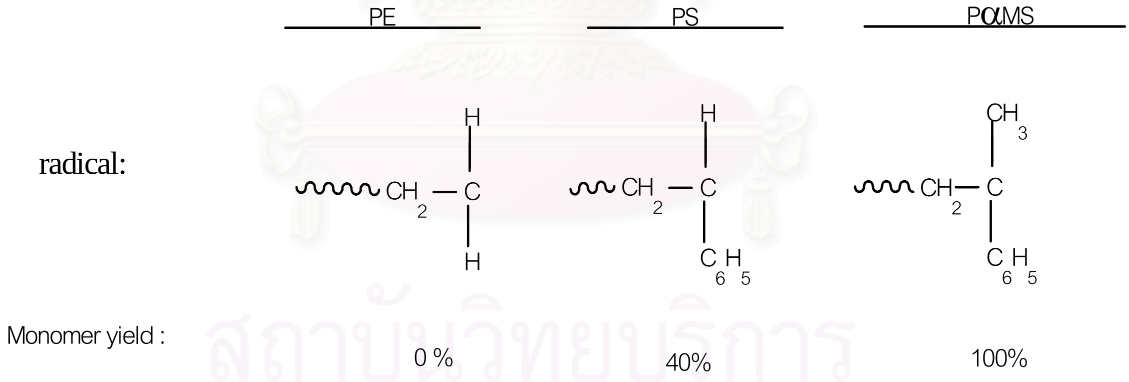
(2.3-3)

or by means of steric factors, as in PMMA. A comparison of the monomer yields in the degradation of PMMA(X=CH_3) and PMA(X=H) shows the importance of the steric hindrance caused by the α̃methyl group:



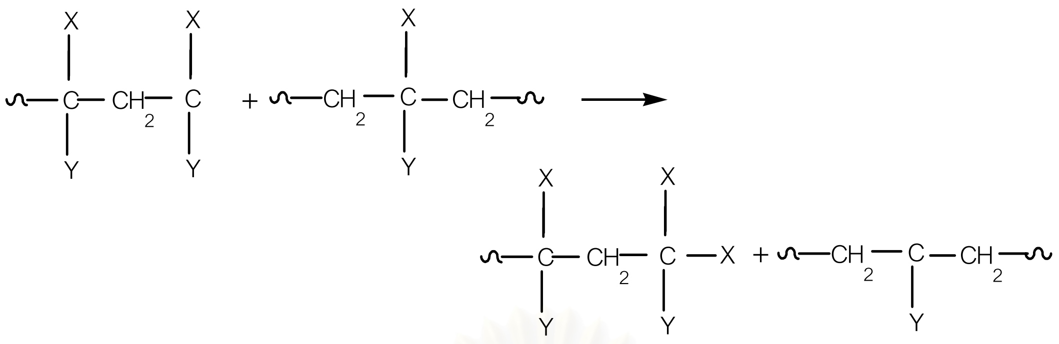
(2.3-4)

The two stabilizing effects can work together as shown in the camparison of monomer yields of polyethylene, PE(X=H, Y=H), PS(X=H, Y=C_6H_5) and poly-$\tilde{\alpha}$methylstyrene, P MS (X=CH_3, Y=C_6H_5):



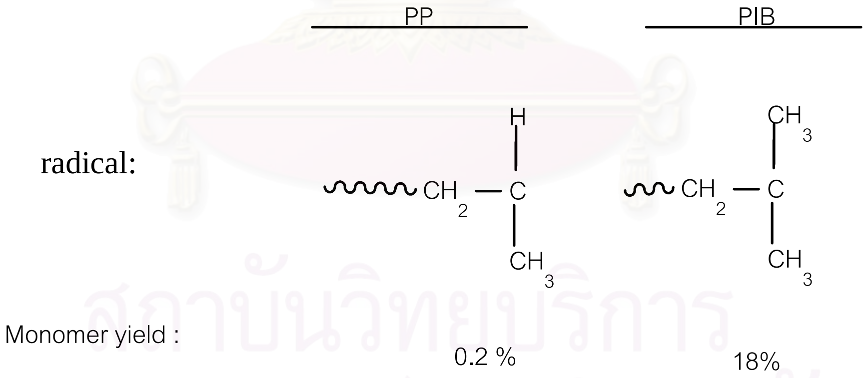
(2.3-5)

A very common way of chain transfer is H-abstraction from another macromolecule(X=H):



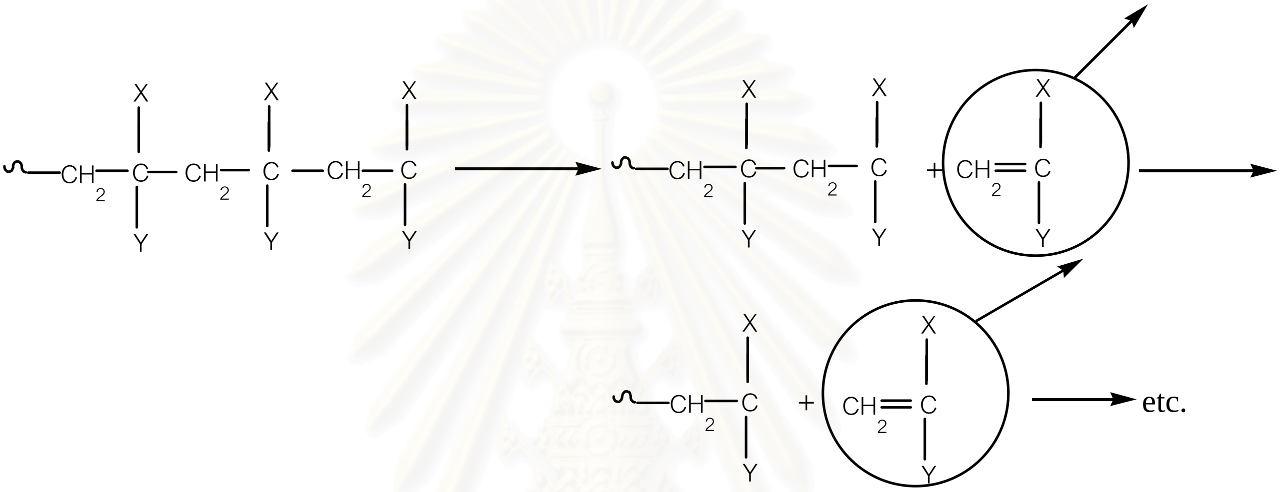
(2.3-6)

Thus, if the polymer does not contain active hydrogens, the probability of chain transfer decreases and that of the depropagation increases. Some examples are shown in (2.3-4) and (2.3-5) working together with other effects; an additional example is the comparison of monomer yields of polypropylene, PP(X=H) and polyisobutylene(X=CH_3):



(2.3-7)

When the above conditions are fulfilled, the terminal radicals will not participate inside



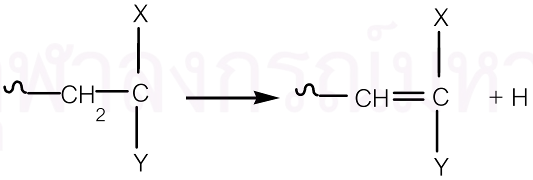
(2.3-8)

reactions but in depropagation steps yielding volatile monomer molecules: However, depropagation requires favorable energetic conditions.

(C) The activation energy of depropagation is the sum of the activation energy of polymerization propagation and the heat of polymerization. The lower of polymerization heat (i.e., the smaller $|\Delta H_P|$), and the lower of the activation energy of depropagation are archived.hus the higher is the probability of depolymerization . While the activation energies of polymerization are of the order of 3-7 kcal/mol, the heats of polymerization are of the order of 3-7 kcal/mol, the heats of polymerization are much higher. For monosubstituted monomers (X=H), - ΔH_P ranges from about 16 to 22 kcal/mol; for disubstituted monomers, from about 8 to 13 kcal/mol. For example, in some of the above-mentioned polymers:

MONOMER	$-\Delta H_P$ (kcal/mol)
Styrene	16.7
α-Methylstyrene	8.4
Methyl acrylate	18.5
Methyl methacrylate	13.3

Depropagation is a β-scission of the terminal radical, producing monomer and a new terminal radical, as shown in reaction (2.3-8). Splitting off of a hydrogen atom by α-scission,

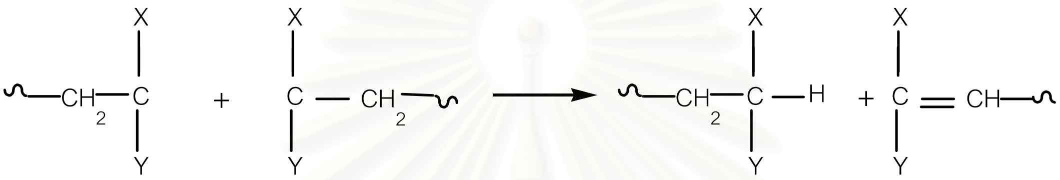


$$\sim CH_2-\underset{Y}{\overset{X}{C}} \longrightarrow \sim CH=\underset{Y}{\overset{X}{C}} + H$$

(2.3-9)

a reaction competitive with depropagation, has a much higher activation energy (by about 10 kcal/mol) than depropagation in cases of disubstituded monomers. In polymers where this difference is not so high, β-scission must be considered as a possible side reaction.

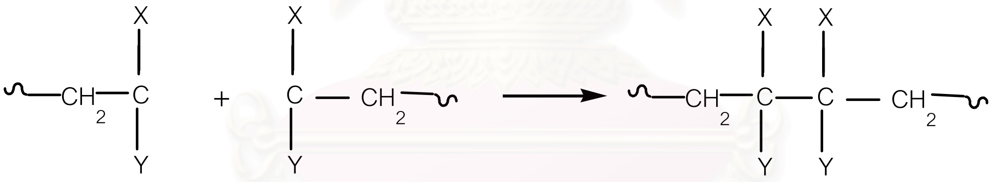
Termination can be a uni- or bimolecular reaction, for example, disproportionation



$$\sim CH_2-\overset{X}{\underset{Y}{C}} + \overset{X}{\underset{Y}{C}}-CH_2\sim \longrightarrow \sim CH_2-\overset{X}{\underset{Y}{C}}-H + \overset{X}{\underset{Y}{C}}=CH\sim$$

(2.3-10)

or recombination:



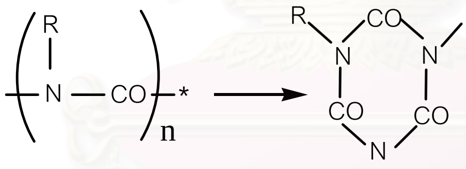
$$\sim CH_2-\overset{X}{\underset{Y}{C}} + \overset{X}{\underset{Y}{C}}-CH_2\sim \longrightarrow \sim CH_2-\overset{X}{\underset{Y}{C}}-\overset{X}{\underset{Y}{C}}-CH_2\sim$$

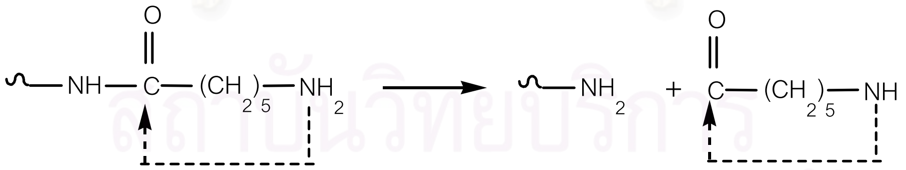
(2.3-11)

If the termination products are of high molecular weight, they do not volatilize and can participate in further reactions. For example, the product of reaction (2.3-10) with unsaturated chain end can react as shown in reaction (2.3-1).

Because of their very low heats of polymerization, polyaldehydes depolymerize virtually quantitatively to monomer. The depolymerization proceeds in the same manner as in the case of the previously presented vinyl polymers. The degradation of polyaldehydes is governed by the the rate of initiation of the depropagation (i.e., the depropagation rate constant is very high). Clearly, any modification of a polymer which would prevent the initiation step of depropagation would stabilize the polymer. Thus, methylation or acetylation of terminal slowing the initiation step of depolymerization. As previously mentioned, copolymers of formaldehyde containing several percent dioxolane are less prone to depolymerization than homopolyformaldehyde because the dioxolane units stops depropagation reaction.

Depending on their structure, polyisocyanates may depolymerize to monomers or forms cylic trimers. Polyisocyanates with aromatic or cyclohexyl substituents are known to depolymerize to monomer when heated to approximately 200 °C. Polyisocyanates having shorts alkyl substituents (R less than five carbons) form cyclic trimers:





Acetylation of the terminal amino groups of nylon 6 substantially decreases the rate of monomer formation when the polymers are subject to temperatures of about 250 °C. This decreased rate of monomer formation suggests that the depropagation step is a back-biting reaction by the amino end groups:

A similar reaction is observed for nylon 7 but only at higher temperatures; this is consistent with the lower thermodynamic stability of eight-membered rings.

The chemical structure of a polymer determines both the type of degradation reaction and the temperature at which the degradation reaction will begin.

Let us first consider the thermal degradation of polymers containing nitrile groups. When polyacrylonitrile is heated to approximately 260-270 ^{o}C, degradation begins via a reaction between nitrile groups of the polymer backbone. As shown in Figure 2.3-12, the reaction between the nitrile groups increases with increasing temperature.

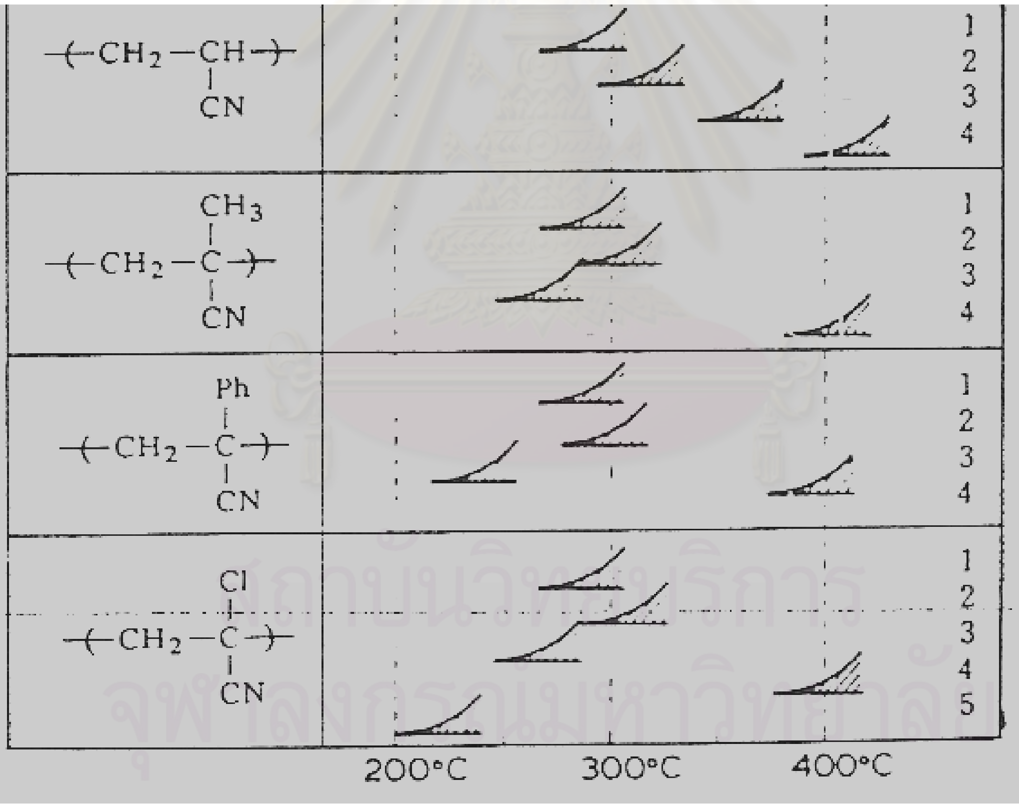


Figure 2.3-12 Temperature ranges of various reactions for the thermal degradation of polymers containing nitrile groups: (1) reactions of the nitrile groups among each other, (2) random degradation, (3) depolymerization, (4) dehydrocyanation, (5) dehydrochlorination.[8]

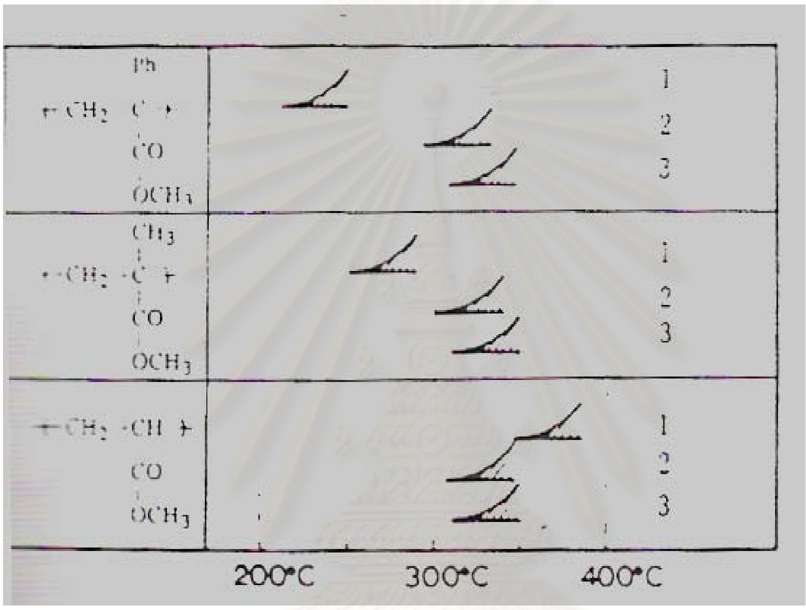
Above 300 ^{o}C, random degradation of the polymer begins to occurs. Depolymerization and dehydrocyanation reactions require very high temperatures. If conditions are such that reactions between nitrile groups predominate, the polyacrylonitrile will eventually lose its original properties due to complete carbonization of the polymer.

The introduction of an α-methyl group in acrylonitrile does not affect the reactions between nitrile groups. The α -methyl group does, however, change the mode of degradation of the polymer. The methyl group causes the temperature at which depolymerization occurs to fall below the temperature necessary for nitrile group reaction; thus, polymethacrylonitrile depolymerizes upon heating to give virtually quantitative yields of monomer.

The tendency for polymethacrylonitrile to depolymerize to monomer is the result of greatly decreased rate of chain transfer due to a lack of α -hydrogen atoms, the higher rate of depropagation resulting from steric hindrance of the disubstituted polymer and the lower bond dissociation energy of carbon-carbon bonds in the polymer backbone.

Because of increased steric hindrance and increased resonance stabilization of its monomer, poly- -phenylacrylonitrile readily depolymerizes at a temperature even lower than poly–α– methacrylonitrile.

Despite its disubstituted structure, poly- α-chloroacrylonitrile behaves differently. As the polymer is heated to near 200 ^{o}C, dehydrochlorination occurs to produce a polyene. The polyene does not depolymerize, but reactions between the nitrile groups can occurs in the polyene as well. The result of nitrile group reactions is a double –stranded polyene. Such materials are quite suitable for carbonization; hence, they are used in the production of “ carbon fibers.” As shown in figures 2.3-13, the polyacrylates behave somewhat differently from the polymethacrylates.



<u>Figure 2.3-13</u> Temperature ranges of various reactions for the thermal degradation of polymers containing an ester group: (1) depolymerization, (2) random degradation. (3) methanol formation.

The presence of an α-methyl group in polymethyl methaacrylate facilitates depolymerization which begins at about 250 ^{o}C. Similarly, α– phenyl groups enhance depolymerization : polymethyl α– phenylacrylate depolymerizes at 220-230 ^{o}C.

Besides various volatile oligomers, methanol is also found in the degradation products of polymethyl acrylate. It is presumed that the ester linkage is stable at the degradation temperature of polymethyl methacrylate but is susceptible to cleavage at the higher degradation temperature (290-300 ^{o}C) of polymethylacrylate.

Although this discussion of the various types of degradation implies that they occur as independent processes, the opposite is often quite true. Many reactions can combine (e.g., via radical intermediates) to cause the observed overall degradation process.

2.3.4 The mechanism of PET depolymerization in methanol by using catalyst [27-28]

Figure 2.3-14 each ester linkage uses a methanol molecule and creates the end groups of a methyl ester and ethylene glycol. Secondary decomposition of the product monomers was neglectable because of the low depolymerization temperature of 433-493 K. At same time, the by product methyl-(2-hydroxyethyl)terephthalate, bis(hydroxyethyl) terephthalate, dimers and oligomers are formed according to the mentioned reaction scheme.

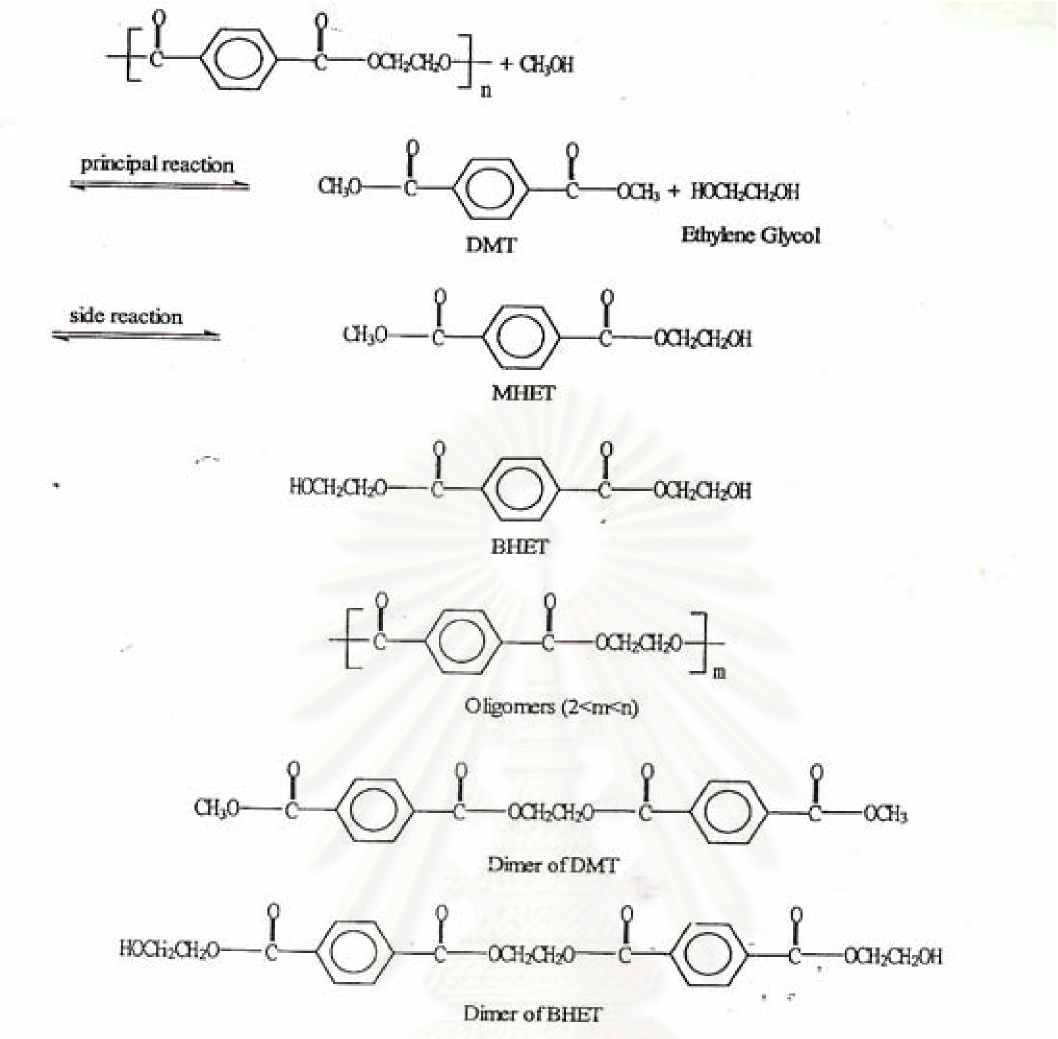


Figure 2.3-14 Overall reaction of PET depolymerization in supercritical methanol

2.4 Kinetics of depolymerization [4-5, 9]

For most kinetic processes, a rate of reaction can be expressed as a product of a temperature-dependent function, k(T), and a composition- or conversion-dependent function, f(X);

$$r = \frac{dX}{dt} = k(T)f(X) \qquad (2.4\text{-}1)$$

where T is the absolute temperature (in K); X is conversion and r is the rate of change of conversion or composition. The temperature-dependent which is the reaction rate constant, is assumed to obey Arrhenius relationship:

$$k(T) = A\exp(-E/RT) \qquad (2.4\text{-}2)$$

where E is the activation energy, A is pre-exponential factor, and R is the universal gas constant. If it is assumed that a simple nth-order kinetic relationship holds for the conversion-dependent:

$$f(X) = (1-X)^n \qquad (2.4\text{-}3)$$

and the quantity (1-X) can be replaced by W, the weight fraction remaining in the depolymerization reaction, then:

$$\ln r = \ln(-dW/dt) = \ln A + n \ln W - (E/RT) \qquad (2.4\text{-}4)$$

If experiment let n is equal to 1, then Equation (2.4-4) becomes:

$$\ln (r/W) = E(-1/RT) + \ln A \qquad (2.4\text{-}5)$$

A slope of plot of ln (r/W) versus [-1/(RT)] will give the activation energy E and intercept equal to ln A.

2.5 Literature Review

In 1998, S.J. Chiu, W.H. Cheng[1] studied the thermal degradation and catalytic cracking of Polyethylene terephthalate. It was investigated at atmospheric pressure. The extent of PET thermal degradation was little affected by the particle size, but tremendiously affected by temperature between 400 and 500 ^oC. In PET catalytic cracking reactions, copper(II)chloride was the most active among tested catalysts. It reduced the carbonaceous residues and increased the percentage weight loss of PET about 3.5 times in comparison with thermal degradation at the same reactions conditions. Considering the weight loss catalyst itself during the reaction, copper(II)chloride was still the most effective. Mixing catalysts and PET by impregnation demonstrated that the effect of temperature on the percentage weight loss was similar to thermal degradation but shortened cracking time. The optimal catalyst-to-PET weight ratio was 0.1.

In 2000, V.M. Castano[2] studied the catalytic depolymerization of Polyethylene terephthalate by using different catalysts, aiming to produce a material suitable for fabricating rigid polyurethane foams. The only catalyst which renders good results is the zinc acetate. It favors the depolymerization reaction up to 230 ^oC. Above this temperature the degradation of PET is so severe that the effect of the catalyst is negligible. The depolymerization reaction was consisted a competition between a depolymerization of the oligomers being formed.

In 2002, Yong Yang and Yijun Lu[3] studied the methanolytic depolymerization of polyethylene terephthalate, the experiment was carried out in a stainless stirred autoclave at temperature of 523-543 K, pressure of 8.5-14.0 MPa, and with a weight ratio of methanol to PET from 3 to 8. The solid product mainly compose dimethyl terephthalate and small amounts of methyl-(2-hydroxyethyl) terephthalate, bis(hydroxyethyl), dimmers and oligomers were analyzed by high performance liquid chromatography(HPLC). The liquid products composed of ethylene glycol and methanol were analyzed by gas chromatography(GC). It was found that both the yield of dimethyl terephthalate and the degree of PET depolymerization were seriously influenced by the temperature, weight ratio of methanol to PET, and reaction time, whilst the pressure has insignificant influence when it is above the critical point of methanol. The optimal depolymerization conditions are temperature of 533-543 K, pressure of 9.0-11.0 MPa, and the weight ratio (methanol to PET) from 6 to 8. The depolymerization of several PET wastes collected from the Chinese market was investigated under the optimal conditions.

Hideki Kurokawa, Masa-aki Ohshima[6] studied Aluminium triisopropoxide(AIP) promoted the methanolysis of polyethylene terephthalate (PET) to form monomers, dimethyl terephthalate (DMT) and ethylene glycol (EG), in an equimolar ratio . The methanolysis at 200 ^{o}C in methanol using an AIP catalyst gave DMT and EG in 64% and 63% yields, respectively. The yields were increased by using a toluene/methanol mixed solvent containing 20-50 volume %toluene; maximum yields, 88% for DMT and 87% for EG, were obtained at 20 volume% toluene.

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Starting material and chemicals

The pure PET materials were commercial chips of fiber grade supplied by Liakzeng company (Bangkok, Thailand).

Analytical grade methanol and other reagents were bought from Fluka chemical Co.,Ltd.

Nitrogen gas (purity 99.5% minimum) was supplied by Enviromate Co., Ltd., Thailand.

3.1.2 Catalysts

Dibutyltin oxide Copper(II)chloride, Zinc acetate and Dimethyl terephthalate were obtained from Fluka chemical Co.,Ltd. and were used without further purification.

3.2 Apparatus

The depolymerization of PET reactions were carried out in a micro-cylindrical reactor, tightly sealed tubing bomb, constructed of stainless steel 316. The micro-reactor had volume capacity of 70 ml. with inside diameter of 30 mm. A needle valve was connected to the top of the tube through which gases could be charged. The reactor was attached to a horizontal motion oscillator and was heated to the desired temperature by a 400 watts heater. The reaction temperature was measured by a sheathed thermocouple attached to the tubing bomb and controlled by a PID temperature controller. The micro-cylindrical reactor and accessories are shown in Figure 3.1 and 3.2, respectively.

3.3 **Experimental procedure**

A Stainless steel micro reactor was heated to the desired temperature reaction by using heater under heating rate of 10 ^{0}C/min. PET methanol and catalyst were charged into the reactor at room temperature. Before heating, to avoid the possible oxidation of PET and products, a small flux of inert gas by N_2, was introduced to the reactor to replace the air. The reactor was heated at temperature of 160-200 ^{0}C, reaction time of 5-40 minutes and catalyst-to-PET weight ratio of 0.3-2%, by weight. After the required time of depolymerization at designed reaction conditions, the reactor was removed from the heater, and quenched in a water-ice bath. The temperature of reaction mixture dropped to under 60 ^{0}C in 1-3 min of quenching. After the reactor vessel was cooled down to about 30 ^{0}C, it was opened and the products in the reactor were then taken out. The mixture was separated into solid and liquid phases by filtration. The flow diagram of the experimental procedure is shown in Figure 3.3.

3.4 Product analysis

Quantitative Analysis

Let

W_D = weight of DMT

W_P = weight of PET

$$\text{Yield of DMT(\%)} = \frac{W_D \times 100}{W_P}$$

3.5 HPLC analysis

After being dried at 323 K to a constant weight, the solid product was mainly composed of Dimethyl terephthalate(DMT) and small amount of methyl-(2-hydroxyethyl)terephthalate(MHET), and then was analyzed with HPLC analysis. HPLC using a Shimadzu LDC-4100 high performance chromatograph (U.S.A) equipped with a reverse-phase Merck-C_8 (4.0x125 mm) column and a SPD-1 ultraviolet detector set at 254 nm. The RP-HPLC procedure was as followings: 20-30 mg/l sample solution used for analysis was prepared by dissolving a certain amount of the dried solid product in a 50:50 (V/V) methanol/ water solution, which was also used as mobile phase with the flow rate of 1 ml/min. The temperature of the column was room temperature (25 ^{o}C). A scanning electron microscope (SEM, Joel JSM 6400) was used for surface observation of the recovered PET conversion.

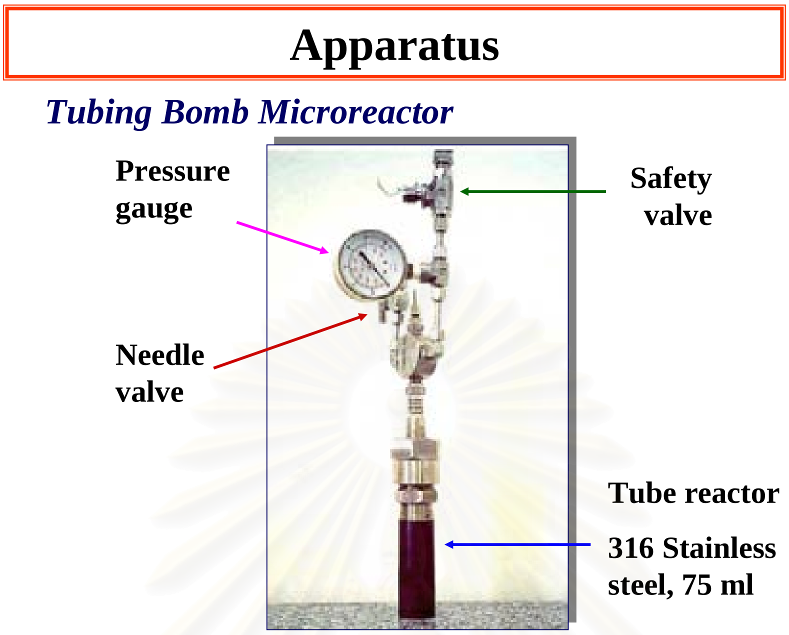


Figure 3.1 Tubing Bomb Microreactor in experiment

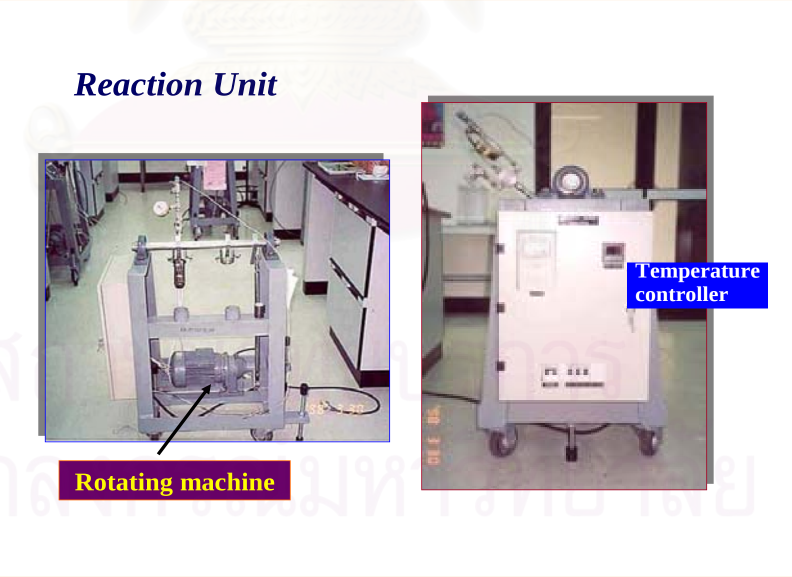
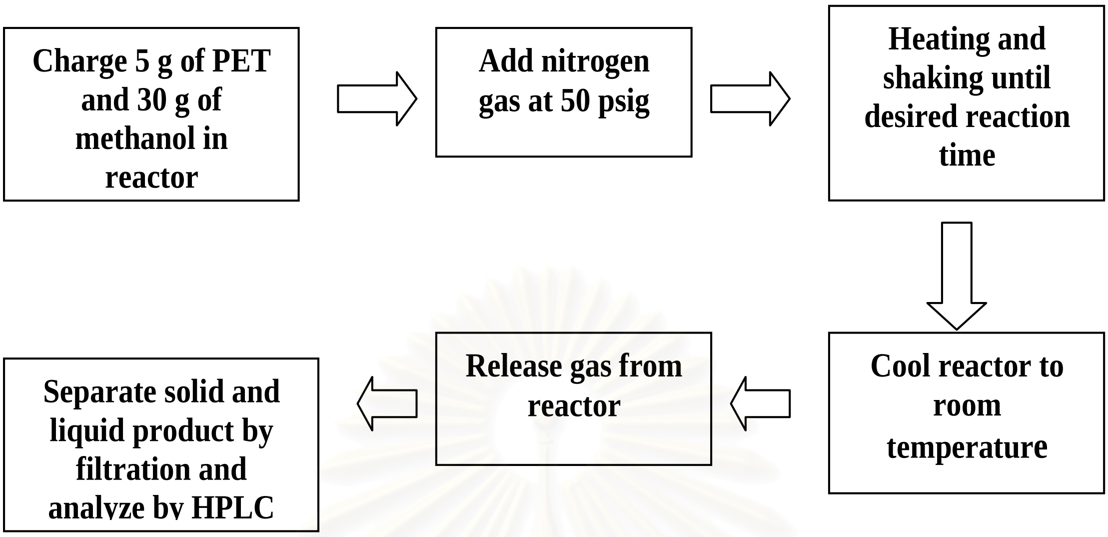


Figure 3.2 The reaction Unit of experiment



<u>Figure 3.3</u> Flow diagram of the experimental procedure

CHAPTER IV

RESULTS AND DISCUSSION

The study of depolymerization of PET by using Cu(II)chloride dibutyltin oxide and Zinc acetate as the catalysts were investigated in three parts as follows:

Part I: Experimental design – a 2^3 factorial design was used to determine the factors that affected the percentage yield of DMT. Those three factors consisted of temperature, amount of catalyst and reaction time. Each factor was presented in two levels.

Part II: The main factors were varied for studying the influence on products yield and composition in liquid products. The optimal depolymerization of PET condition was found in this part.

Part III: Kinetic study – kinetic parameters, order of reaction and activation energy, were investigated.

4.1 Experimental design and analysis [29-36]

The effects of interesting factors were determined by an experimental design 2^k factorial method. The chosen factors for this experiment were temperature, reaction time and catalyst-to-PET weight ratio. This study consisted of three factors: A, B, and C at two levels whose design is called a 2^3 factorial design. In addition, it used the “+ and –” to represent the low and high levels of the factors respectively, and the eight runs in a 2^3

design as shown in Table 4.1. This is sometimes called the design matrix which we wrote the treatment combinations in a standard order as (1), a, b, ab, c, ac, bc and abc.

The considered factor levels were based on the condition in the reviewed literature [3, 6].The low and high levels of the temperature were 160 ^{o}C, and 230 ^{o}C respectively. The 5 and 40 minutes were determined to the low and high levels of reaction time, whereas catalyst-to-PET weight ratio 0.3 % and 2 % were investigated to the low and high levels respectively. Table 4.2 shows factors, coded factors, and the factor levels of each experiment.

Table 4.1 The design matrix and labels of treatment combinations.

Run	A	B	C	Labels
1	-	-	-	(1)
2	+	-	-	a
3	-	+	-	b
4	+	+	-	ab
5	-	-	+	c
6	+	-	+	ac
7	-	+	+	bc
8	+	+	+	abc

Table 4.2 Factors, coded factors and factor levels for the depolymerization of PET by using Cu(II)chloride dibutyltin oxide and zinc acetate as the catalysts

Factor	Coded factor	Factor levels	
		Low (-)	High (+)
Temperature (^{o}C)	A	160	220
Reaction time (minute)	B	5	40
Percentage of catalyst (wt%)	C	0.3	2

The table of plus and minus signs for the contrast constants and the yield of DMT from depolymerization of PET over Cu(II)chloride catalyst was shown in Table 4.3 From these contrasts, it may be estimated the 7 factorial effects and the sum of squares by using the percentage yield of DMT obtained from the depolymerization of PET by Cu(II)chloride dibutyltin oxide and zinc acetate as the catalysts shown in Table 4.4.

The normal probability plot of these effects is shown in Figure 4.1. All of the effects that lie along the straight line were negligible, whereas the large effects were far from the line. The important effects that emerge from this analysis were the main effects of A, and C and the BC interaction.

The analysis of variance (ANOVA) and F-test at 95% confidence were used to confirm the magnitude of main effects as shown in Table 4.5. The statistical F-tests were used to determine the significance of effects. The sum of squares of the effects and that of the error were calculated, and then the resulting F-values (F_{exp}) were calculated. For any factors to be statistically significant, the absolute value of F_{exp} should be greater than the F-value (F_{tab}) obtained from the standard F-distribution with a 95% confidence.

Table 4.3 The contrast constant for a 2^3 factorial design experiment from the depolymerization of PET by using Cu(II)chloride as the catalyst

	Effect			Condition				
Treatment	A	B	C	Temperature(A) (^oC)	Time(B) (minute)	%Cu(II)chloride C	Run No.	Cu(II)chloride yield (solid)
1	-	-	-	170	5	0.3	3	0
a	+	-	-	220	5	0.3	4	65.34
b	-	+	-	170	40	0.3	7	30.13
ab	+	+	-	220	40	0.3	1	85.52
c	-	-	+	170	5	2	8	17.12
ac	+	-	+	220	5	2	2	70.23
bc	-	+	+	170	40	2	6	34.13
abc	+	+	+	220	40	2	5	92.24

Table 4.4 The summary of effect estimates for the depolymerization of PET reaction by using Cu(II)chloride as the catalyst

Factor	Effect Estimate	Sum of Squares	%Contribution
A	57.99	6725.10	84.97
B	22.33	997.48	12.60
C	8.18	133.91	1.69
AB	-1.24	3.06	0.04
AC	-2.38	11.31	0.14
BC	-2.82	15.93	0.20
ABC	3.74	27.94	0.35
	SS total	7914.73	

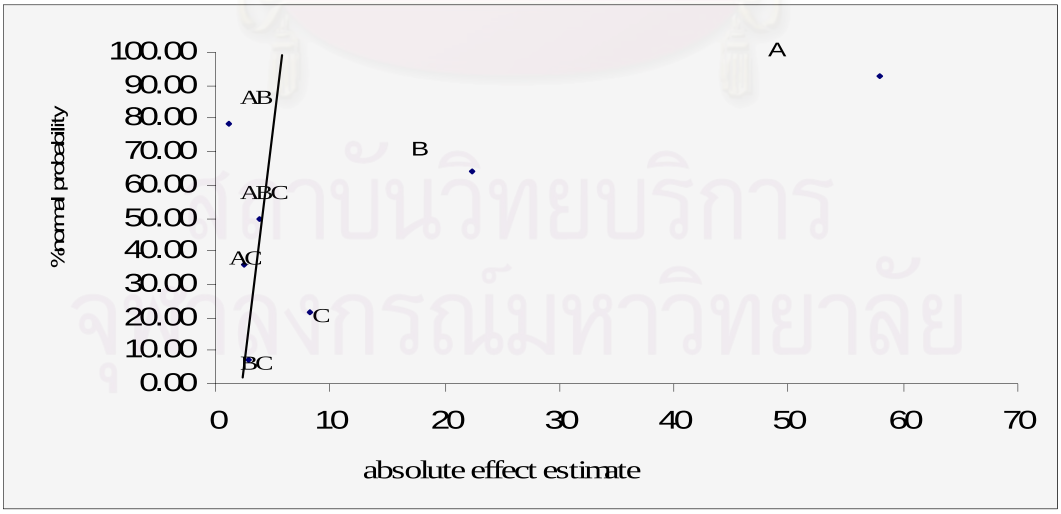


Figure 4.1 The normal probability plot of the effects for the 2^3 factorial in depolymerization of PET by using Cu(II)chloride

Table 4.5 Analysis of Variance for the depolymerization of PET reaction by using Cu(II)chloride as the catalyst

Source of Variance	Sum of square	Degree of Freedom	Mean square	Fo	$F_{0.025,1,4}$
A:temperature	6725.10	1	6725.10	461.89	>12.22
B:time	997.48	1	997.48	68.51	>12.22
C:catalyst content	133.91	1	133.91	9.20	>12.22
Error	58.24	4	14.56		
Total	1011.59	7			

From the analysis of variance in Table 4.5, F_{exp} of the main effects A and B were greater than the F_{tab}. It can be concluded that main effects, namely A (temperature) and B (reaction time) significantly affected the percentage yield of DMT, whereas the main effect, C (catalyst content) insignificantly affected the percentage yield of DMT from the depolymerization of PET by using Cu(II)chloride as the catalyst.

In the same way, the contrast constant and the yield of DMT, the factor effect estimate and the analysis of variance were illustrated from Table 4.6 to Table 4.11, and Figure 4.2 and Figure 4.3 for the depolymerization of PET by using dibutyltin oxide and zinc acetate as the catalyst.

Table 4.6 The contrast constant for a 2^3 factorial design experiment from the depolymerization of PET by using dibutyltin oxide as the catalyst

Run	Effect			Condition			dibutyltin oxide
	A	B	yield (solid) 0	Temperature (^{o}C)	Time (minute)	%dibutyltin oxide	
1	-	-	74.44	160	5	0.3	0
2	+	-	52.15	210	5	0.3	74.44
3	-	+	88.52	160	40	0.3	52.15
4	+	+	12.34	210	40	0.3	88.52
5	-	-	97.08	160	5	2	12.34
6	+	-	63.15	210	5	2	97.08
7	-	+	82.06	160	40	2	63.15
8	+	+	+	210	40	2	82.06

Table 4.7 The summary of effect estimates for the depolymerization of PET reaction by using dibutyltin oxide as the catalyst

Factor	Effect Estimate	Sum of squares	%contribution
A	53.62	5749.14	65.23
B	25.51	1301.01	14.76
C	9.88	195.23	2.22
AB	25.98	1349.40	15.31
AC	1.79	6.41	0.07
BC	7.61	115.82	1.31
ABC	6.94	96.33	1.09
	SS total	8813.34	

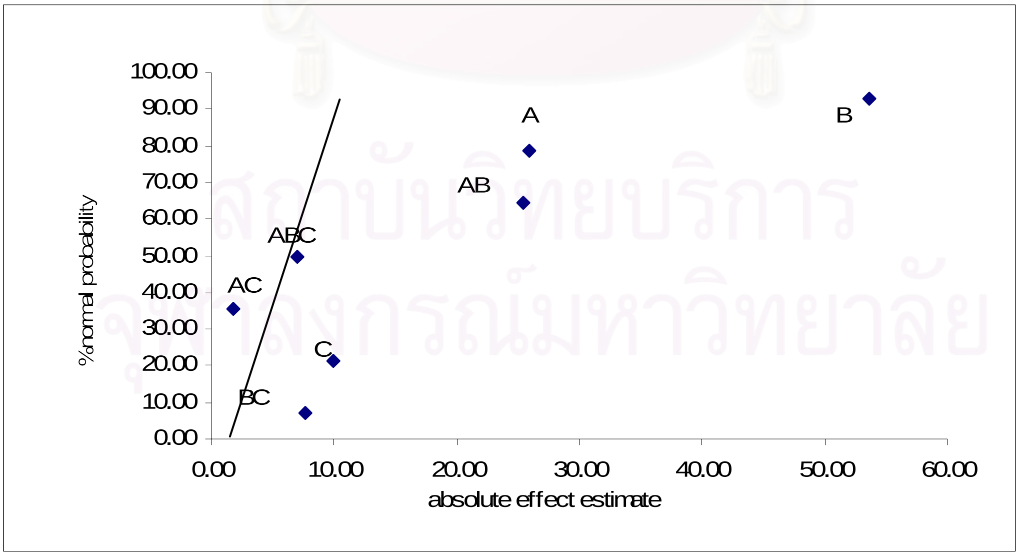


Figure 4.2 The normal probability plot of the effects for the 2^3 factorial in depolymerizationof PET by using Dibutyltin oxide catalyst

Table 4.8 The analysis of variance for the depolymerization of PET reaction by using dibutyltinoxide as the catalyst

Source of Variance	Sum of square	Degree of Freedom	Mean square	Fo	$F_{0.025,1,4}$
A:temperature	5749.14	1	5749.14	78.91	>12.22
B:time	1301.01	1	1301.01	17.86	>12.22
C:catalyst content	195.23	1	195.23	2.68	>12.22
AB	1349.4	1	1349.4	18.52	>12.22
Error	218.56	3	72.853		
Total	8813.34	7			

Table 4.9 The contrast constant for a 2^3 factorial design experiment from the depolymerization of PET by using zinc acetate as the catalyst

	Condition			
Run	Temperature(A) (°C)	Time(B) (minute)	%Zinc acetate (C)	Zinc acetate %yield (solid)
1	170	5	0.3	0
2	220	5	0.3	65.04
3	170	40	0.3	47.73
4	220	40	0.3	87.56
5	170	5	2	15.67
6	220	5	2	94.23
7	170	40	2	60.36
8	220	40	2	96.24

Table 4.10 The summary of effect estimates for the depolymerization of PET reaction by using Zinc acetate as the catalyst

Factor	Effect Estimate	Sum of squares	% contribution
A	54.83	6012.11	67.07
B	29.24	1709.66	19.07
C	16.54	576.13	6.43
AB	16.97	547.31	6.11
AC	2.40	11.45	0.13
BC	5.88	69.33	0.77
ABC	4.36	38.15	0.43
	SS total	8964.14	

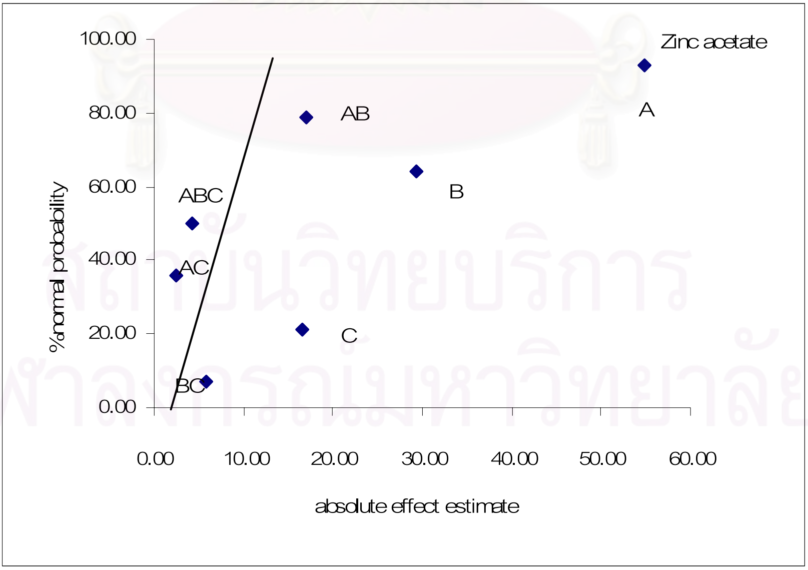


Figure 4.3 The normal probability plot of the effects for the 2^3 factorial in depolymerizationof PET by using Zinc acetate

Table 4.11 The analysis of variance for the depolymerization of PET reaction by using Zinc acetate as the catalyst

	Sum of square	Degree of Freedom	Mean square	Fo	F0.025,1,4
A:temperature	6012.11	1	6012.11	151.66	>12.22
B:time	1709.66	1	1709.66	43.13	>12.22
C:catalyst content	576.13	1	576.13	14.53	>12.22
AB	547.31	1	547.31	13.81	>12.22
Error	118.93	3	39.643		
Total	8964.14	7			

From the analysis of variance as shown in Table 4.8 and 4.11, the main effects that influence the percentage yield of DMT obtained from the depolymerization of PET by using dibutyltin oxide and zinc acetate were temperature (A) and reaction time (B). These results were similar to that of the depolymerization of PET by using Cu(II)chloride as the catalyst. The interaction effect of AB insignificantly affected percentage yield of DMT.

Then, the depolymerization of PET was performed at various temperatures from 160 °C to 210 °C, the reaction time of 5-40 min, and the catalyst-to-PET weight ratio 0.3-2 wt % for the univariate experiment.

Part II: Univariate study for depolymerization of PET by using catalyst

4.2 The effect of time and temperature on depolymerization of PET

1% dibutyltin oxide was used to depolymerize PET in a reactor of 70 CC. under N_2 atmosphere in the range of temperature 160^0C to 190^0C. Figure 4.4 and 4.5 show the evolution of DMT with temperature and time. From the Figure 4.4 at the time of 5-10 min and the temperature of 160 ^{0}C, the yield of DMT was not found. In addition, if the experiment was allowed to go on to over 35 min, the graphs were nearly stable since the thermal energy of 160 ^{0}C was so little that bond of polymer cannot be broken down. This caused the rate of reaction slow down and stable. At the temperature ranging from 170 ^{0}C to 190 ^{0}C, the percentage yield of DMT had increased as by the time, and PET had mostly been converted to DMT at 20 minutes. Considering Figure 4.5, at the time of 5-10 min, the percentage yield of DMT had risen when the temperature had been increased, while at the time of 15-40 min, the percentage yield of DMT varied according to the temperature ranging from 160 ^{0}C to 170 ^{0}C. However, the time factor had little impact on the percentage yield of DMT at the temperature of 170 ^{0}C onwards. It can be explained that the cumulative thermal energy was high enough to break down the bond of polymer, so the reaction was occurred rapidly and stable when most of PET was converted to DMT.

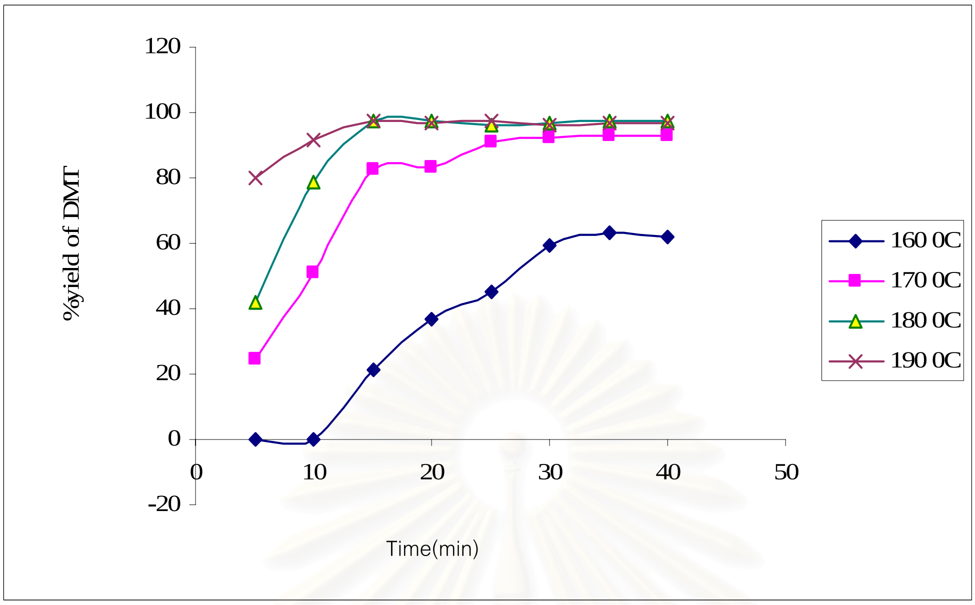


Figure 4.4 The effect of reaction time on yield of DMT(%) using dibutyltin oxide catalyst at temperature of 160-190 ^{o}C and catalyst-to-PET 1% by weight

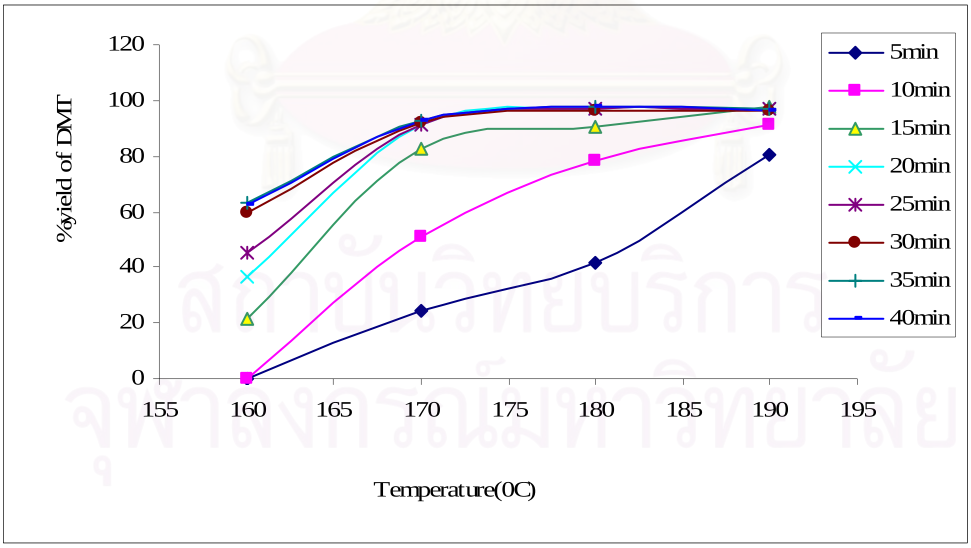


Figure 4.5 The effect of reaction temperature on yield of DMT(%) using dibutyltin oxide catalyst at the time of 5-40 min and catalyst-to-PET 1% by weight.

1% Cu (II) chloride was used to depolymerize PET in a reactor of 70 CC. under N_2 atmosphere in the range of temperature 170 ^{0}C to 210 ^{0}C. Figure 4.6 and 4.7 showed the evolution of DMT with temperature and time. From the Figure 4.6 at the time of 5-10 min and the temperature of 170 ^{0}C, the yield of DMT was not found. In addition, if the experiment was allowed to go on to over 35 min, the graphs were nearly stable since the thermal energy of 170 ^{0}C was so little that bond of polymer cannot be broken down. This caused the rate of reaction slow down and stable. At the temperature ranging from 180 ^{0}C to 190 ^{0}C, the percentage yield of DMT had increased as by the time, and PET had mostly been converted to DMT at 20 minutes. As a result, the percentage yield of DMT began to be constant, while at the temperature of 200 and 210 ^{0}C, the percentage yield of DMT had increased as by the time, and PET had been mostly converted to DMT at 15 minutes. Consequently, from over 15 minutes, the time factor had no effect on the percentage yield of DMT. It can be explained that the cumulative thermal energy was high enough to break down the bond of polymer, so the reaction was occurred rapidly and stable when most of PET was converted to DMT.

According to figure 4.7, at the time of 5 min and 10 min, with the temperature ranging from 170 ^{0}C to 180 ^{0}C, just small amount of PET had been converted to DMT. Nevertheless, after that time the percentage yield of DMT had increased according to an increase in temperature. At the time of 15 min and 20 min, the percentage yield of DMT had increased as time went by, and started to remain constant at the temperature of 200 ^{0}C, while at the time of 25 min and 30 min, the temperature factor had an effect on the percentage yield of DMT at the temperature ranging from 170 ^{0}C to 180 ^{0}C, but after that it had no impact on the percentage yield of DMT of the reaction.

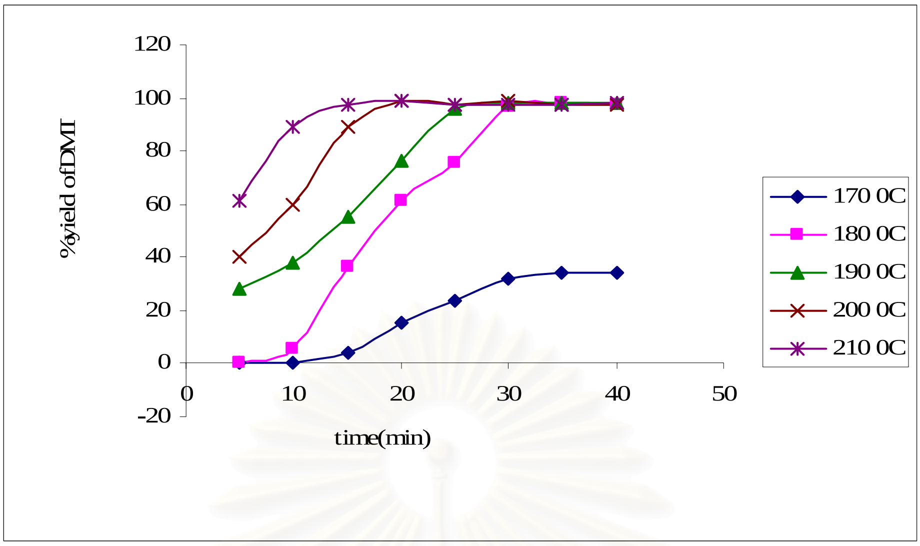


Figure 4.6 The effect of reaction time on yield of DMT(%) using Cu(II)chloride catalyst at temperature of 170-210 ^{o}C and catalyst-to-PET 1% by weight

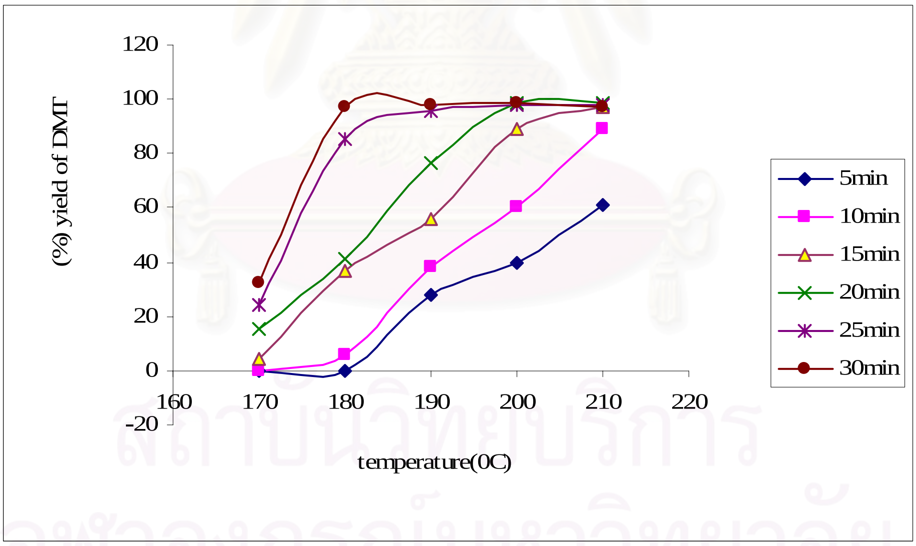


Figure 4.7 The effect of reaction temperature on yield of DMT(%) using Cu(II)chloride catalyst at the reaction time of 5-30 min and catalyst-to-PET 1% by weight.

Zinc acetate was used to depolymerize PET in a reactor of 70 CC. under N_2 atmosphere in the range of temperature 170 ^{0}C to 210^{0}C. Figure 4.8 and 4.9 showed the evolution of DMT with temperature and time. From the Figure 4.8 at the time of 5-10 min and the temperature of 170 ^{0}C, the yield of DMT was not found. In addition, if the experiment was allowed to go on to over 35 min, the graphs were nearly stable since the thermal energy of 170 ^{0}C was so little that bond of polymer cannot be broken down. This caused the rate of reaction slow down and stable. At the temperature ranging from 180 ^{0}C to 190 ^{0}C, the percentage yield of DMT had increased as time went by, and PET had mostly been converted to DMT at 25 minutes. As a result, the percentage yield of DMT began to be constant, while at the temperature of 200 and 210 ^{0}C, the percentage yield of DMT had increased as time went by, and PET had been mostly converted to DMT at 15 minutes. Thus, from more 15 minutes, the time factor had no effect on the percentage yield of DMT. It can be explained that the cumulative thermal energy was high enough to break down the bond of polymer, so the reaction was occurred rapidly and stable when most of PET was converted to DMT.

From figure 4.9, at the time of 5 min, 10 min, and 15 min with the temperature ranging from 170 ^{0}C to 180 ^{0}C, just small amount of PET had been converted to DMT. However, after that time the percentage yield of DMT had increased according to an increase in temperature, while at the time of 20 min onwards, the temperature factor had an effect on the percentage yield of DMT at the temperature ranging from 170 ^{0}C to 180 ^{0}C, but at the temperature more 180 ^{0}C, the temperature factor had no impact on the percentage yield of DMT of the reaction.

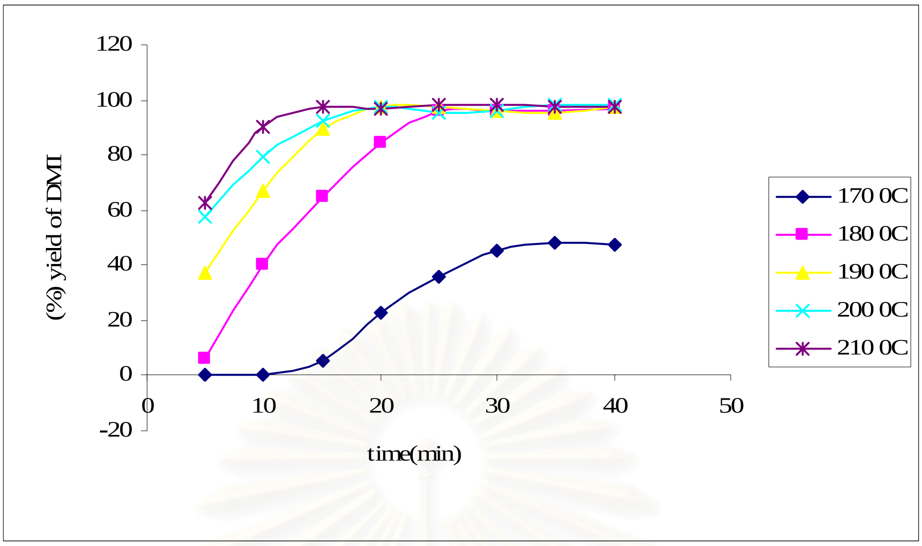


Figure 4.8 The effect of reaction time to yield to DMT(%) with Zinc acetate catalyst at temperature of 170-210 °C and catalyst-to-PET 1% by weight

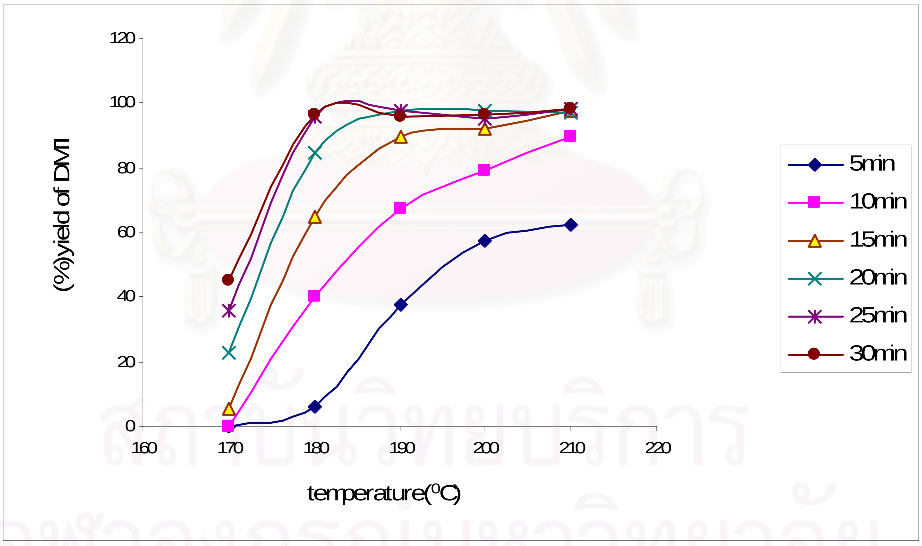


Figure 4.9 The effect of reaction temperature on yield of DMT(%) using zinc acetate catalyst at the reaction time of 5-30 min and catalyst-to-PET 1% by weight.

From the experiment using three catalysts: dibutyltin oxide, Cu(II)chloride, and Zinc acetate, the results were compared shown in Table 4.12 and Figure 4.10 ranging under the temperature of 160-190 ^{0}C, the reaction time of 20 minutes, 1 % by weight of each catalyst. Figure 4.10 shows that the yield of DMT began to be constant when dibutyltin oxide had been used as a catalyst at the temperature higher than 170 ^{0}C, and the reaction time of 20 minutes. While the constant yield of DMT occurred when Cu(II) chloride had been used as a catalyst at the temperature higher than 190 ^{0}C, and the reaction time of 20 minutes, the zinc-acetate-catalyst experiment caused the same result at the temperature higher than 180 ^{0}C, and the reaction time of 20 minutes.

Table 4.12 The comparison of the DMT percentage yield among three different catalysts in the depolymerization of PET at the reaction time of 20 min and weight of 1%catalyst

Temperature(^{o}C)	Percentage of DMT yield		
	Dibutyltin oxide	Cu(II)chloride	Zinc acetate
160	36.56	0	0
170	90.54	15.30	23.12
180	97.26	61.00	84.50
190	96.81	76.22	97.74

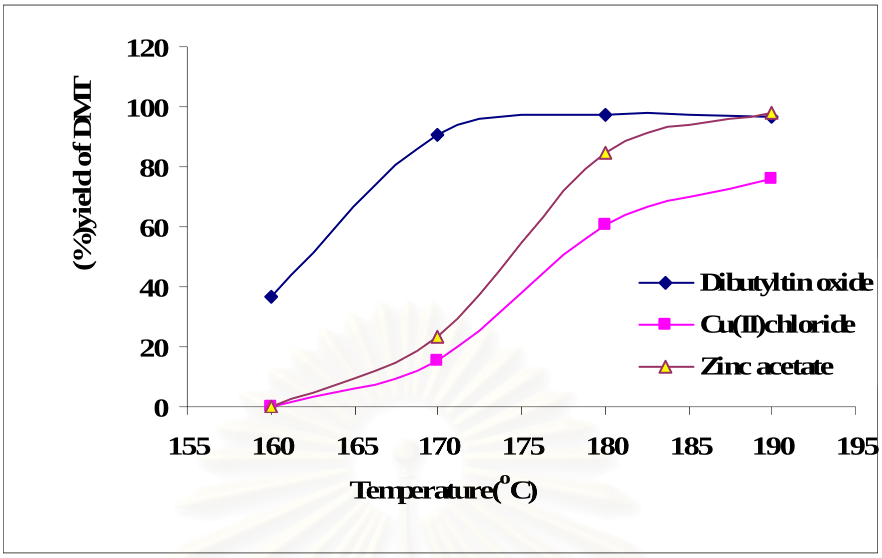


Figure 4.10 The comparison of the DMT percentage yield in the depolymerization of PET using three different catalysts at the reaction time of 20 min and the weight of 1% catalyst

From the study, the effect of time and temperature on depolymerization of PET, determined that temperature and time affect the reaction significantly at the temperature range of 170 ^{0}C-190 ^{0}C. This could be explained that thermal energy enhances the breaking down of polymer bond as well as reducing the viscosity of the solution used in the reaction. Thus, the catalyst accelerates the reaction more easily. At the temperature higher than 190 ^{0}C, the rate of reaction decreases, since PET was used up rapidly (converted to DMT). Additionally, the error could be occurred in the heat-up period (about 5 minutes) of 180 ^{0}C to 190 ^{0}C due to the depolymerization of PET can be happened in this period.

4.3 The effect of catalyst-to-PET weight ratio on depolymerization of PET.

Dibutyltin oxide Cu(II)chloride and Zinc acetate were used to depolymerize PET in a reactor of 70 CC. under N_2 atmosphere at the temperature of 180 ^{o}C and reaction time of 30 min for dibutyltin oxide and temperature of 200 ^{o}C and reaction time of 30 min for Cu(II)chloride and Zinc acetate catalyst were shown in Table 4.13. From the Figure 4.11 the yields of DMT versus the percentage catalyst by weight ratio of 0.3, 0.5, 0.8, 1 and 2, it is found that when the amount of these three mentioned catalysts had been increased, the percentage yield of DMT had slightly increased as well. For example, when dibutyltin oxide had been used as a catalyst in the depolymerization of PET, the result shows that an increase in the catalyst caused a rise in percentage yield of DMT. However, at the level of 1% and 2% of the catalyst and the temperature of 180 ^{0}C, the percentage yield of DMT began declining since the depolymerization of PET which had been converted to DMT product started decreasing, but the reaction began converting PET to other less–molecular-weighted monomer products instead. As a result, there was a reduction in percentage yield of DMT. All in all, when the weight ratio of dibutyltin oxide catalyst was 0.8% the extent of the yield of DMT was 97% and weight ratio of Cu(II)chloride catalyst was 1% the yield of DMT was 98% and ratio of Zinc acetate catalyst was 0.5% the yield of DMT was 96%.

Table4.13 The effect of catalyst-to-PET weight ratio on depolymerization of PET

percentage of catalyst	Percentage of DMT yield		
	dibutyltin oxide	Cu(II)chloride	Zinc acetate
	180 ^{0} C, 30 min	200 ^{0}C, 30min	200 ^{0}C, 30min
0.3	65.42	82.2	79.67
0.5	82.10	85.9	96.21
0.8	97.26	92.12	90.31
1	90.11	98.55	87.63
2	82.06	90.14	82.52

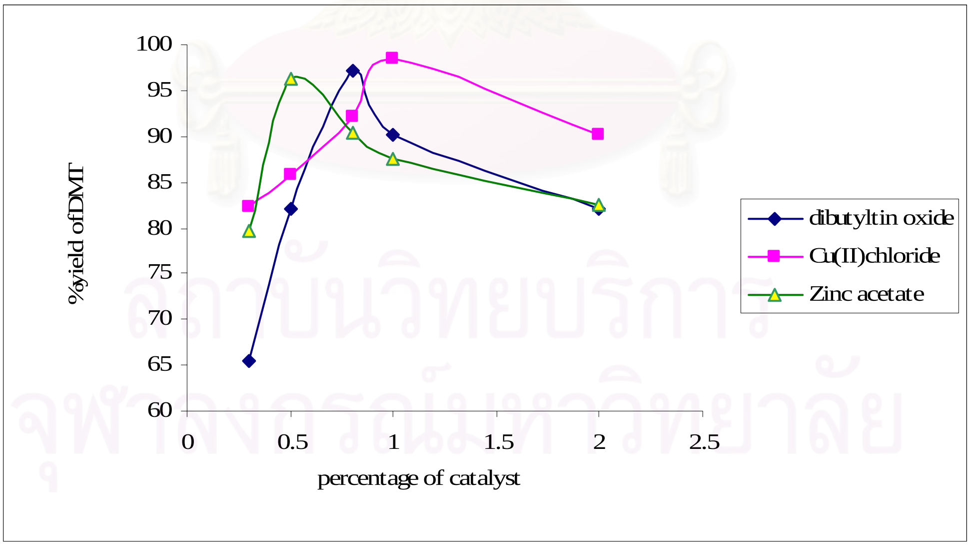


Figure 4.11 The effect of catalyst-to-PET weight ratio on depolymerization.

From the results of the depolymerization reaction, it is found that the amount of three mentioned catalysts, namely Dibutyltin oxide, Cu(II)chloride and Zinc acetate had little impact to the reaction. Nevertheless, compared to the non-catalyst reaction or inactive-catalyst reaction, adding these three above-mentioned catalysts helped improving the reaction considerably. The comparison between the results of three-catalyst reaction and the previous results of the reactions with various other catalysts or a non-catalyst reaction is shown in Table 4.14, it is found that the three catalysts helped increases the activity of the reaction substantially[1]. It, thus, caused the reduction of time and temperature using in the reaction.

Table4.14 The comparison between the results of three-catalyst reaction with various other catalysts and a non-catalyst reaction

Catalyst	Condition		%yield of DMT
	Temperature (^oC)	Time (min)	
Dibutyltin oxide	180	15	97
Cu(II)chloride	190	25	95
Zinc acetate	190	20	97
Aluminium triisopropoxide [Hideki, 6]	200	120	64
None [Yong Yang, 3]	270	40	99

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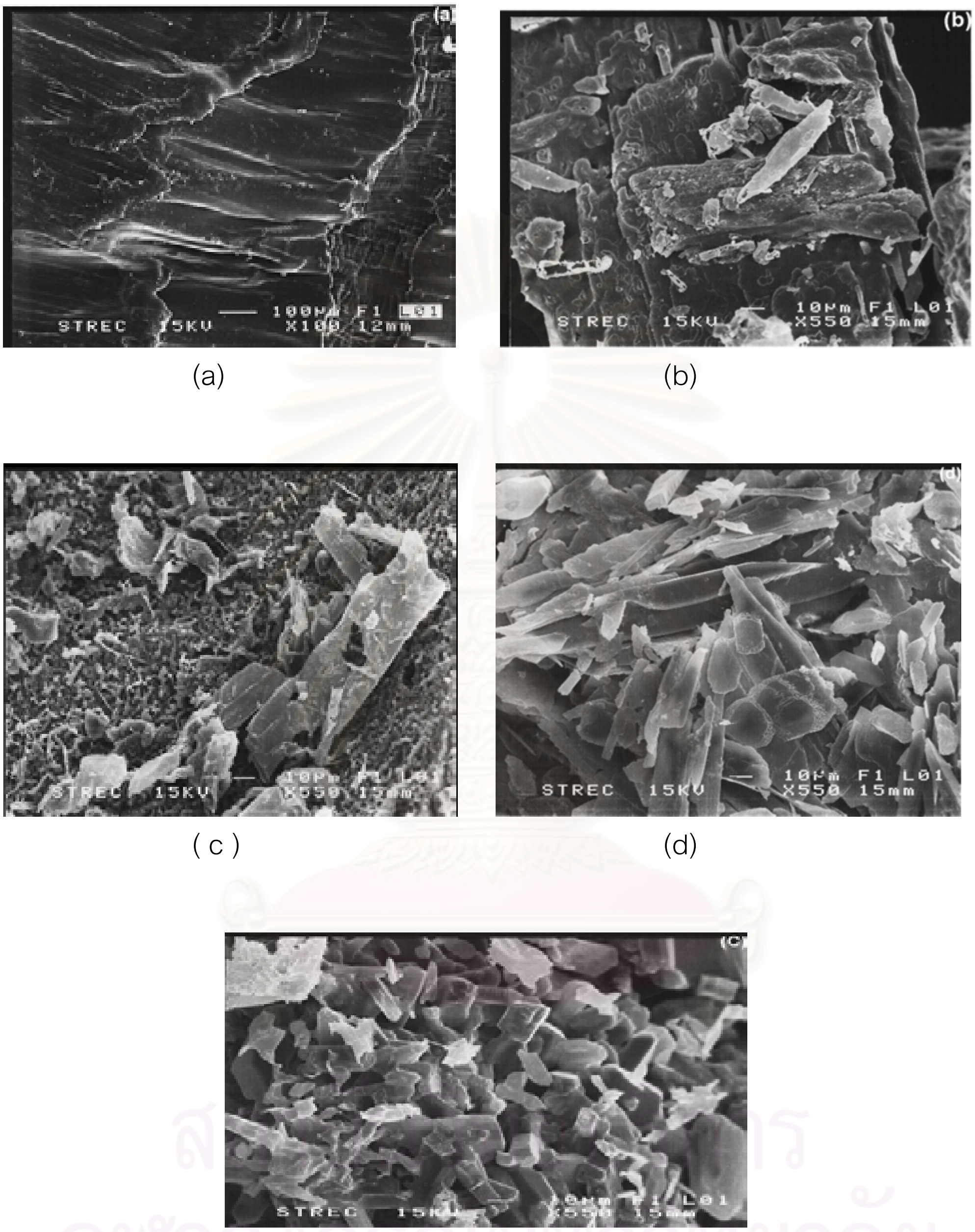
[1] Activity of the reaction means increasing the rate of reaction toward equilibrium without being appreciably consumed in the process.

SEM Micrograph of the depolymerization of PET reaction was shown on the figure 4.12. PET material (Figure 4.12 (a)) began gradually breaking at 5 min. (Figure 4.12 (b)). According to Figure 4.12 (c), PET had increasingly broken after 10 min then at 15 min, PET had been converted to DMT (Figure 4.12(d)). Comparing to DMT sample (Figure 4.12 (e)), we deduced that PET started its conversion at 170 ^{0}C with 0.8 % dibutyltin oxide catalyst.

In addition, we have also conducted the HPLC analysis of DMT's component in the solid product as shown in Figure 4.13(a)-(c). Under the condition of 170 ^{0}C, 1% wt of catalyst, with different time periods (10, 15, and 25 min.), and the amount of DMT's component had been increasing by the time when time passed. The further results showed that the amounts of oligomers were negligibly small, and the main product was DMT's monomer. The depolymerization of PET (without catalyst) at the temperature of 230 ^{0}C and the reaction time of 25 min was shown in Figure 4.13(d). As shown in the Figure 4.13(d)-(e), the non-catalyst reaction generated the higher amounts of oligomers than those from the dibutyltin-oxide-catalyst reaction. It can be concluded that the dibutyltin oxide catalyst caused the reduction of the reaction temperature and enhanced the level of selectivity on the main product.



(a) (b)

(c) (d)

(e)

Figure 4.12 SEM show Depolymerization of PET reaction (a) The sample of PET material.(b), 5 min.(c) 10 min (d) 15 min at 170 ^{0}C, 1% dibutyltin oxide e)The sample of DMT material.

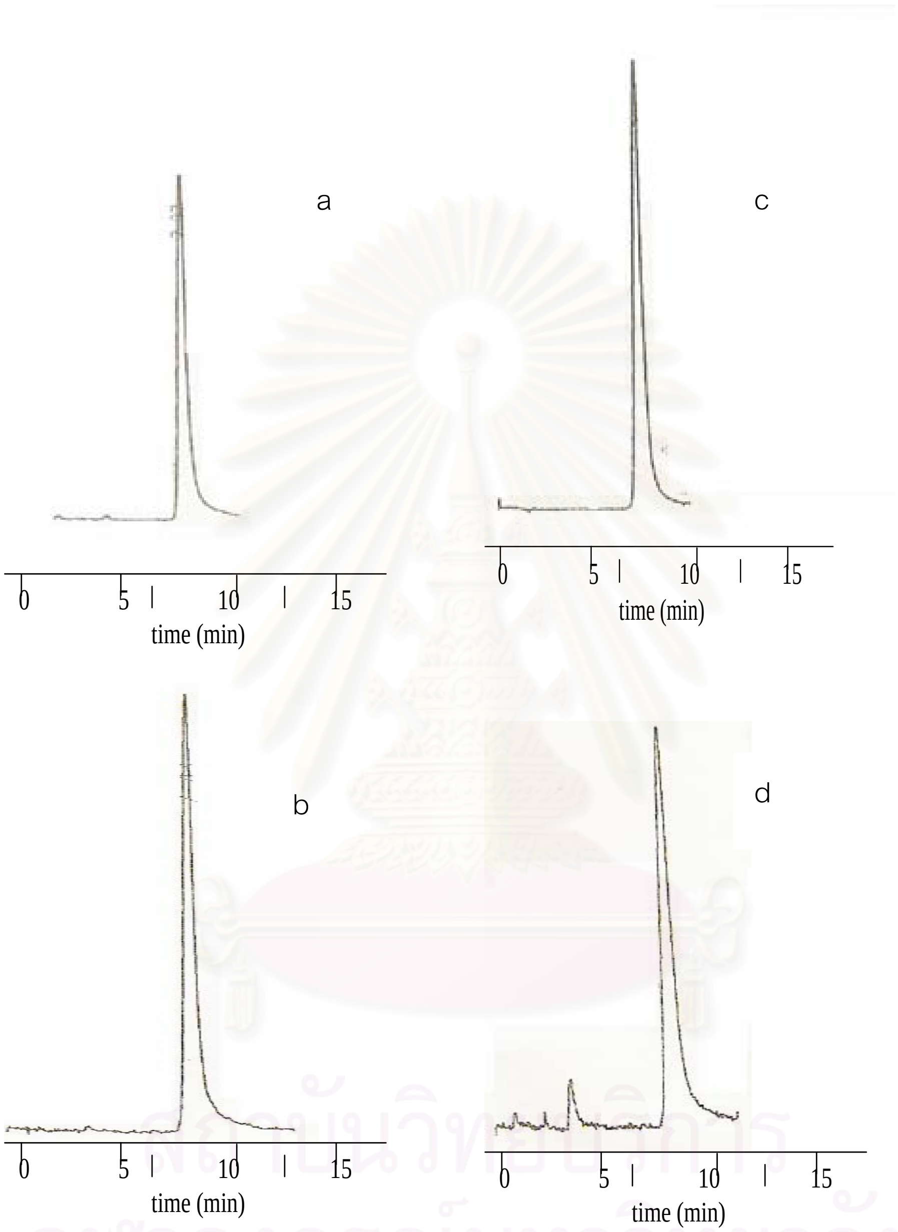


Figure4.13 HPLC chromatogram of DMT product after depolymerization of PET different reaction time, (a) 10 min(b)15 min (c) 25 min at 170 ^{0}C, 1% wt. of dibutyltin oxide catalyst (d) the non-catalyst reaction at the temperature of 503 K and the reaction time of 25 min.

4.4 Part III: The Calculation of Kinetic Parameters

Catalysts is used to depolymerize PET in a reactor of 70 CC. under N_2 atmosphere in the range of temperature 160 ^{0}C - 200 ^{0}C and the reaction time 5-20 minutes. Equation (2.4-4) has been used for the calculation of kinetic parameters of the depolymerization of PET. Table 4.15 - 4.17 and Figure 4.14-4.16 based on the experiments using dibutyltin oxide Cu(II) chloride and Zinc actetate as catalysts respectively in the mathematical form of the relationship between ln [(-dW/dt/W] and [-1/RT] indicates that its slope is equal to activation energy, and its intercept is equivalent to ln A. Their graph plot for this method is in the form of a linear ‘first order’ reaction for the depolymerization of PET.

Table 4.15 Results for kinetics of Depolymerization for PET by using dibutyltin oxide catalyst.

10 min	dw	dt	dw/dt	W	1/RT	ln[(-dw/dt)/w]
160 ^{0}C	1	5	0.2	1	-0.00028	-1.60
170 ^{0}C	0.26	5	0.052	0.49	-0.00027	-2.20
180 ^{0}C	0.37	5	0.074	0.21	-0.00027	-1.05
190 ^{0}C	0.55	5	0.11	0.09	-0.00026	0.20

15min	dw	dt	dw/dt	W	1/RT	ln[(-dw/dt)/w]
160 ^{0}C	0.21	5	0.042	0.79	-0.00028	-2.94
170 ^{0}C	0.32	5	0.064	0.17	-0.00027	-0.98
180 ^{0}C	0.09	5	0.018	0.12	-0.00027	-1.9
190 ^{0}C	0.06	5	0.012	0.03	-0.00026	-0.92

20 min	dw	dt	dw/dt	W	1/RT	ln[(-dw/dt)/w]
160 ^{0}C	0.16	5	0.032	0.63	-0.00028	-2.97
170 ^{0}C	0.08	5	0.016	0.09	-0.00027	-1.73
180 ^{0}C	0.08	5	0.016	0.04	-0.00027	-0.92

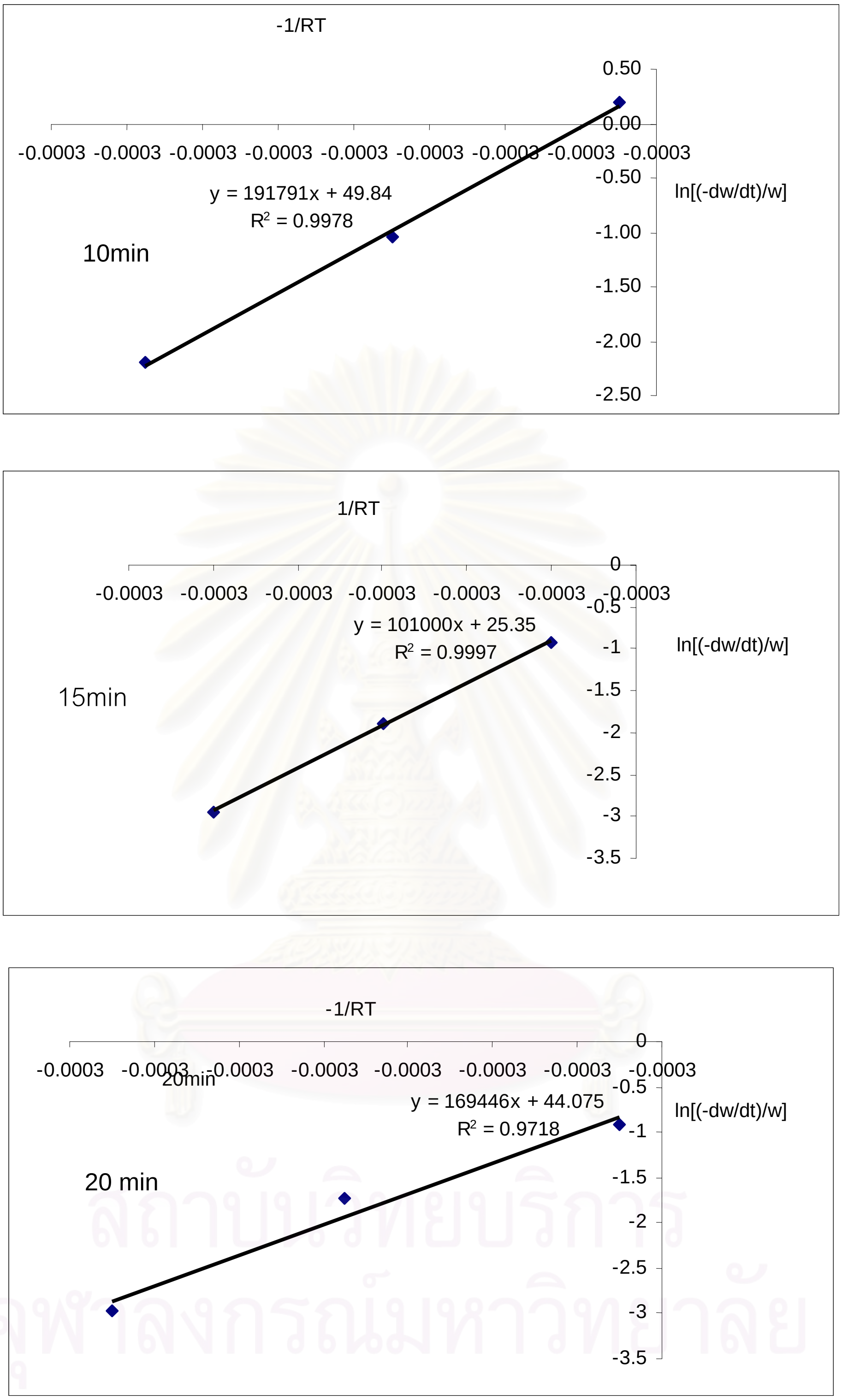


Figure 4.14 (a) – (c) First order kinetic plot of depolymerization of PET under various time periods by using dibutyltin oxide catalyst.

Table 4.16 Results for kinetics of Depolymerization for PET by using Cu(II)chloride catalyst.

10min	dw	dt	dw/dt	W	1/RT	ln[(-dw/dt)/w]
180 ^{0}C	0.06	5	0.012	0.94	-0.00027	-4.34
190 ^{0}C	0.2	5	0.04	0.52	-0.00026	-2.56
200 ^{0}C	0.2	5	0.04	0.4	-0.00025	-2.3
210 ^{0}C	0.28	5	0.056	0.11	-0.00025	-0.68

15min	dw	dt	dw/dt	W	1/RT	ln[(-dw/dt)/w]
170 ^{0}C	0.04	5	0.008	0.96	-0.00027	-4.7
180 ^{0}C	0.3	5	0.06	0.64	-0.00026	-2.53
190 ^{0}C	0.18	5	0.036	0.44	-0.00025	-0.64
200 ^{0}C	0.29	5	0.058	0.11	-0.00025	-0.62

20 min	dw	dt	dw/dt	W	1/RT	ln[(-dw/dt)/w]
170 ^{0}C	0.11	5	0.022	0.85	-0.00027	-3.65
180 ^{0}C	0.25	5	0.05	0.39	-0.00027	-2.12
190 ^{0}C	0.2	5	0.04	0.24	-0.00026	-1.77
200 ^{0}C	0.1	5	0.02	0.01	-0.00025	0.69

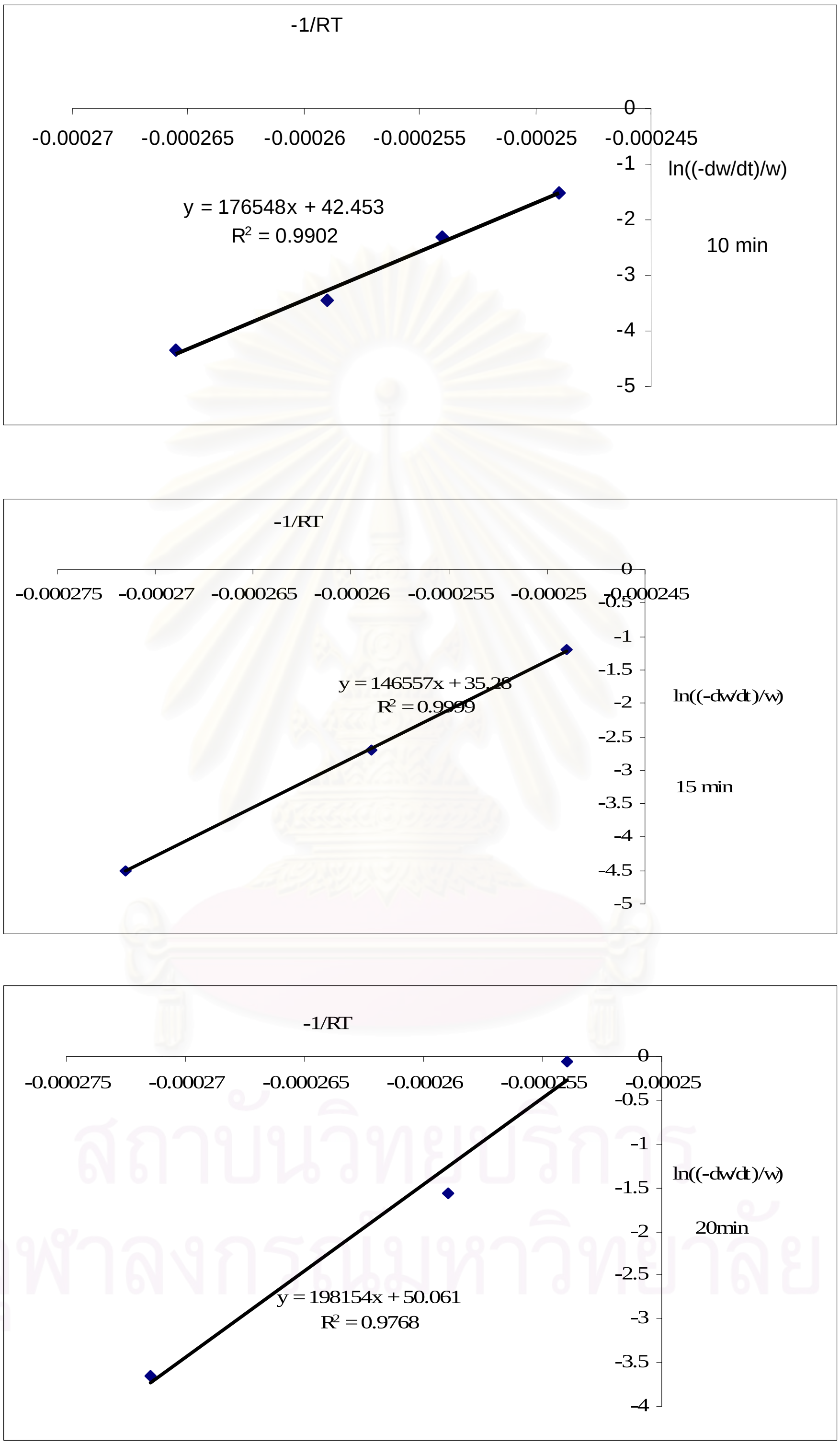


Figure 4.15 (a) – (c) First order kinetic plot of depolymerization of PET under various time periods by using Cu(II)chloride catalyst.

Table 4.17 Results for kinetics of Depolymerization for PET by using Zinc acetate catalyst.

10min	dw	dt	dw/dt	W	1/RT	ln[(-dw/dt)/w]
170 ^{0}C	0	5	0	1	-0.00027	-2.5
180 ^{0}C	0.34	5	0.068	0.6	-0.00026	-1.4
190 ^{0}C	0.29	5	0.058	0.13	-0.00025	-0.52
200 ^{0}C	0.32	5	0.064	0.11	-0.00025	-0.62

15min	dw	dt	dw/dt	W	1/RT	ln[(-dw/dt)/w]
170 ^{0}C	0.05	5	0.01	0.95	-0.00027	-3.3
180 ^{0}C	0.11	5	0.022	0.49	-0.00026	-2.1
190 ^{0}C	0.13	5	0.026	0.1	-0.00025	-1.5
200 ^{0}C	0.03	5	0.006	0.08	-0.00025	-2.4

20min	dw	dt	dw/dt	W	1/RT	ln[(-dw/dt)/w]
170 ^{0}C	0.18	5	0.036	0.77	-0.00027	-3.8
180 ^{0}C	0.23	5	0.046	0.16	-0.00026	-2.1
190 ^{0}C	0.03	5	0.006	0.07	-0.00025	-1.3
200 ^{0}C	0.03	5	0.006	0.02	-0.00025	-0.05

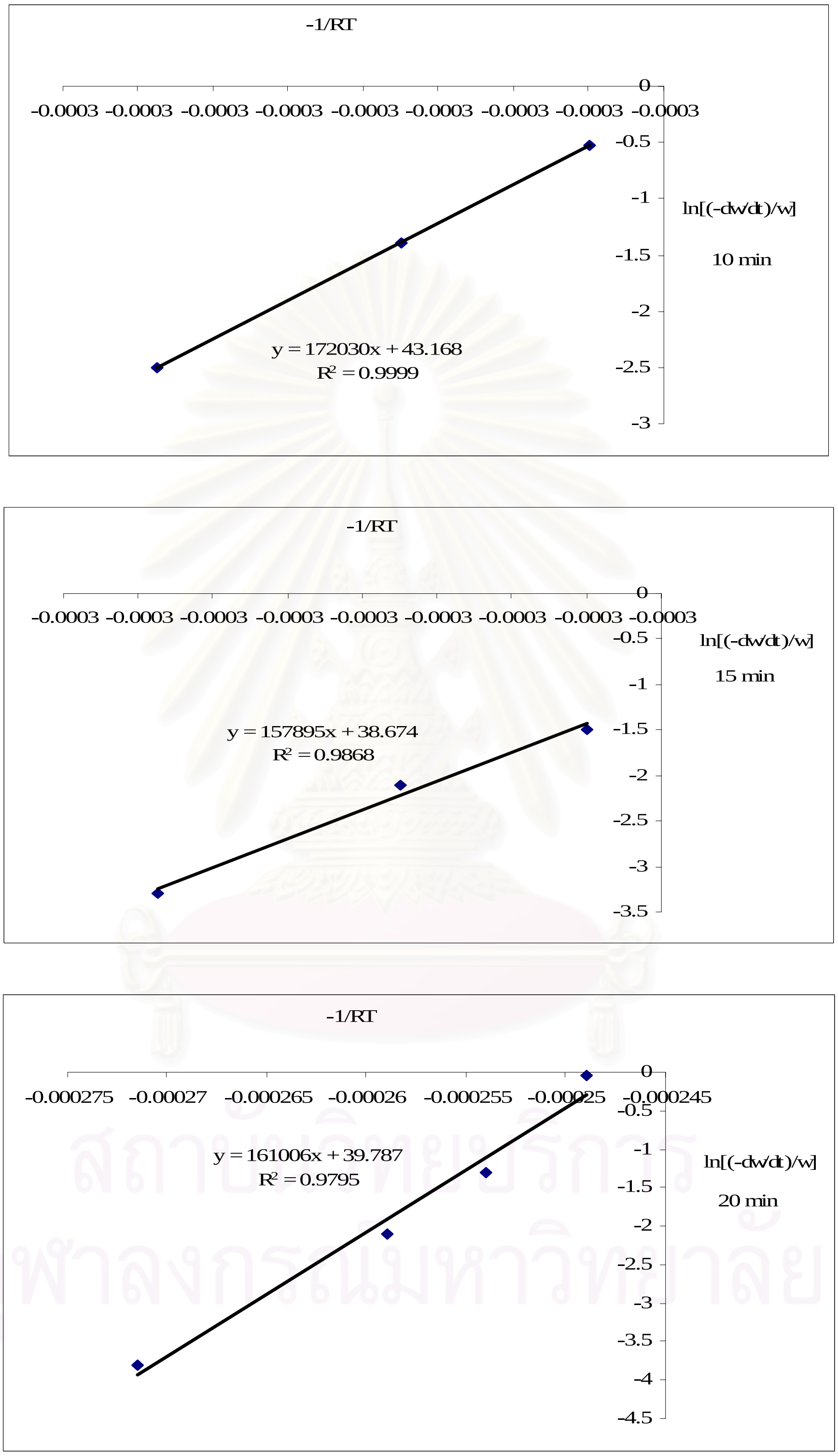


Figure 4.16 (a) – (c) First order kinetic plot of depolymerization of PET under various time periods by using Zinc acetate catalyst.

Figure 4.14-4.16 (a) – (c), indicates the values of activation energy under various time periods. Figure 4.14-4.16 (b) clearly shows that its value had declined, for the catalyst helped supporting the reaction rate, and thus reducing the activation energy (minimum energy that is required to make the reactants collide). Nonetheless, when the reaction went on for a certain period of time, the reaction rate began diminishing, and caused an increase in the activation energy at 15-20 min (Figure 4.14 (c)) due to the depletion of the reactant. In addition, the average value of activation energy for each catalyst calculated from Table 4.18. The activation energy was less in the reaction of depolymerization of PET using catalysts due to the effect of the added catalysts that promotes the reaction opportunity to the reactants. As the results of those, the required temperature and time would be decreased. In addition, the catalysts also increased the selectivity to the products.

Table4.18 Comparing for each catalyst and none catalyst to kinetics of Depolymerization results for PET

Catalyst	Temperature (^0C)	Time (minute)	Activation energy (KJ/mol)	Pre-exponential(A)
Dibutyltin oxide	160-190	5-10	191.70	4.41E+21
	160-190	10-15	101.00	1.02E+21
	160-180	15-20	169.45	1.39E+19
average			**154.05**	
Cu(II)	170-200	5-10	176.59	1.09E+22
Chloride	170-200	10-15	146.56	1.02E+21
	170-200	15-20	198.15	2.23E+25
average			**173.77**	
Zinc acetate	170-200	5-10	172.03	5.60E+18
	170-200	10-15	157.89	6.22E+16
	170-200	15-20	161.01	1.91E+17
average			**163.64**	
	260-300	5-10	195.04	6.54E+19
None	260-300	10-15	190.32	2.14E+17
[Yong yang, 3]	260-300	15-20	243.80	8.93E+18
average			**209.72**	

4.5 Depolymerization of PET wastes

Under the optimal depolymerization conditions, we have also investigated the depolymerization of waste film and used bottle flakes of several main brand beverage bottles in Thailand's market. The depolymerization of PET wastes was carried out for 25 min at the conditions of 180 ^{0}C, and the weight of dibutyltin oxide catalyst 1%. The results of depolymerization are summarized in Table 4.19. It indicates that the various PET wastes can be well depolymerized under the optimal reaction condition. The color and the source had no distinct influence on the depolymerization.

Table 4.19 Results of Depolymerization for different PET wastes at 180 ^{0}C, for 25 min with dibutyltin oxide catalyst 1%

PET waste	%yield of DMT
500-ml mineral water bottle (Perrier vittel Co.Ltd., Ayuttaya city)	97.70
500-ml Crystal water bottle (Sermsuk Co.Ltd., Nakornsawan city)	98.45
500-ml Aura natural mineral (Thoranee pipat Co.Ltd., Chiangmai city)	96.17

Kurokawa[6] reported results of GPC analysis for depolymerization of PET. The average molecular weights (Mn and Mw) of recovered PET were determined by GPC for investigating the details of methanolysis, and Figure 17 shows the GPC curves. Average molecular weight of the starting PET was Mn = 16,000, and its distribution was Mw/Mn = 3.4 [Figure 17(a)]. After methanolysis at 200 ^{0}C in the absence of catalyst, PET was recovered as chips (Figure 17(b)) with a small amount of powder. Mn of the powder portion (4300) was nearly equal to that of the chips (5500) and about one-third lower than that of the starting PET. The molecular weight distributions of both powder and chips became sharp in comparison with that of the initial PET. These findings suggest that, when Mn is above 4000, depolymerization does not take place at random positions of the polymer chain. When methanolysis was carried out in the presence of the catalyst, most PET was depolymerized to the monomers and 12.3% for the initial charge was recovered. Mn of the recovered PET was equal to 2200 and its GPC curve tailed to low molecular weight [Figure17c, Mw/Mn = 2.6]. This means the occurrence of depolymerization at random positions on the polymer chain.

The results of GPC analysis suggest that the methanolysis in the absence of a catalyst includes at least two steps represented in Figure16. In the first step of methanolysis, the chain length of PET was shortened to about 1/3 [Figure18]. Even when the catalyst is not used, the first step takes place easily [Figure18(I)]. The details of this step are not well understood, however the polymer chain might be cut off at a tie molecule because such molecules exist in an amorphous part of PET and have high accessibility. Collins and Zeronian [16] reported similar results for alkaline hydrolysis of fabric PET; after the hydrolysis, crystalline material was deposited on the fibre surface, and its molecular weight was approximately 2400.

The second step [Figure18 (II)], the formation of monomers from oligomers, is promoted only in the presence of catalyst and the monomers were produced in high yield. Those result suggest that the catalyst promotes the formation of monomers.

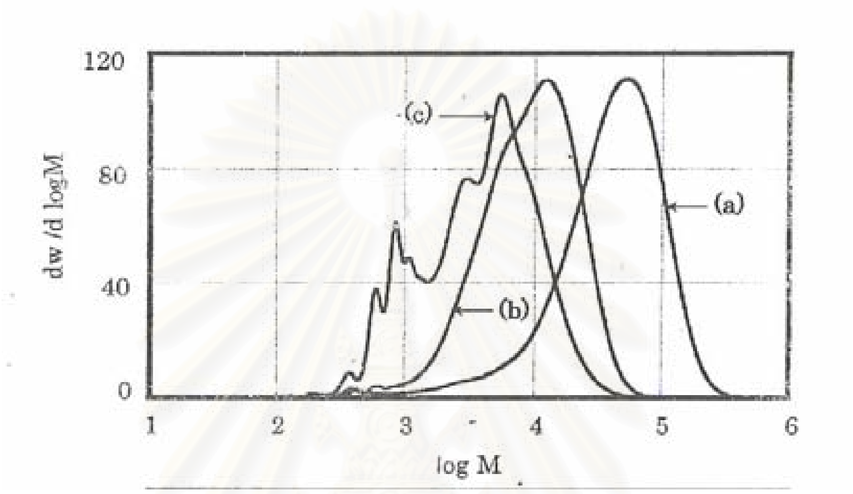


Figure4.17 GPC curves of PET recovered after methanolysis. Before methanolysis (a). After methanolysis in methanol (b) at 200 ^{0}C in the absence of catalyst, and (c) at 200 ^{0}C in the presence of catalyst.

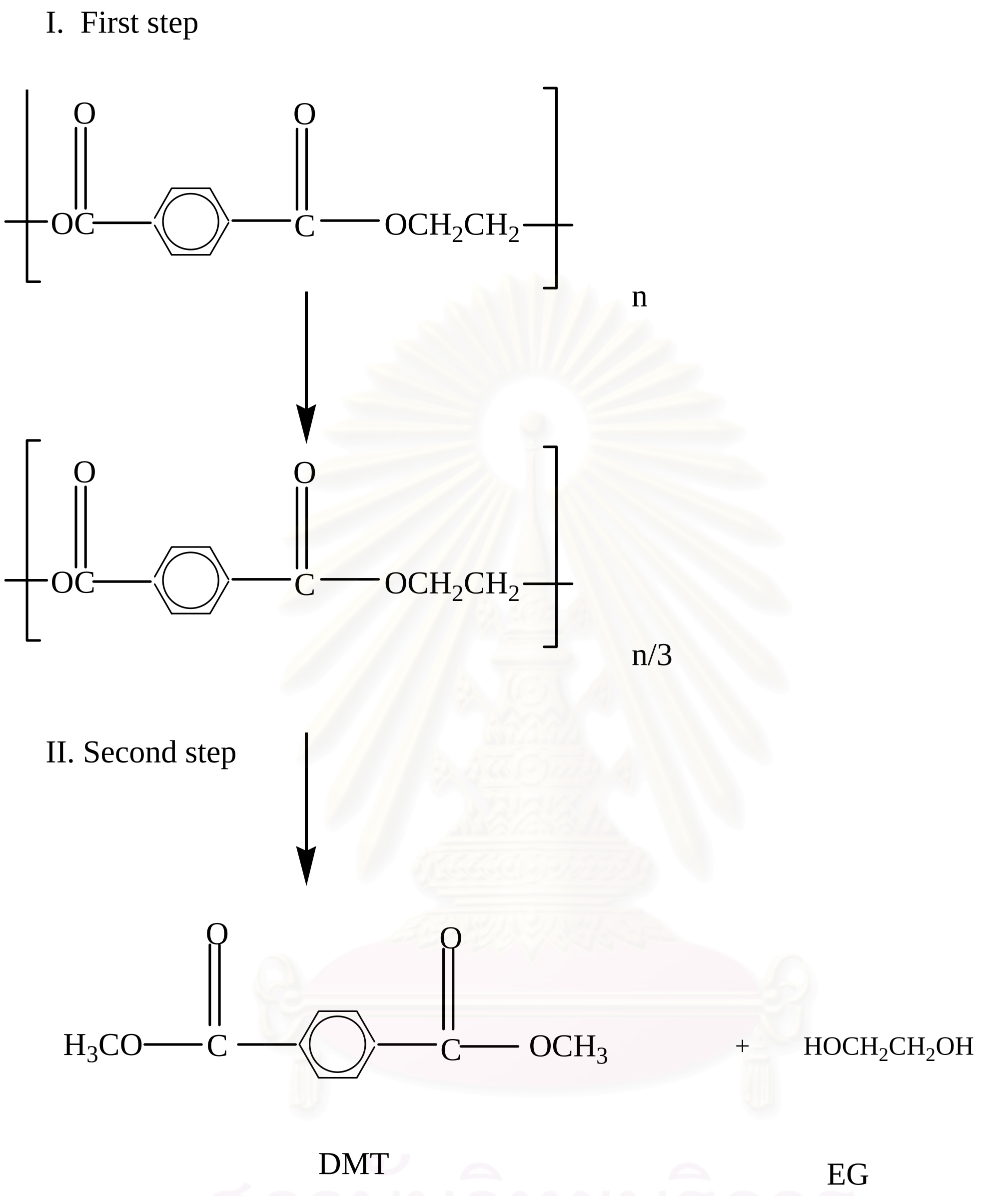


Figure4.18 Reaction scheme of PET methanolysis.

Additionally, comparing with the result in the reviewed literature [12-13], it can be concluded that dibutyltin oxide, was active and selective to depolymerization of PET and also lower the condition of the experiment as shown in Table 4.20.

Table 4.20 The comparison of the results of reviewed literatures

	Condition				
researcher	Temperature (^{o}C)	Time(min)	catalyst	% yield of DMT	Activation Energy(KJ/mol)
Yang Y.and et.al [3]	270	30	none	99	209.72
Kurokawa H. and et.al [6]	200	120	aluminium triisopropoxide	87	-
Ibrahim J.M.	400	60	none	78	243.8
This study	180	15	dibutyltin oxide	97	154.05

CHAPTER V

CONCLUSIONS

The treatment of waste plastic products by depolymerization of PET by using catalyst has some advantages over thermal degradation (noncatalytic method). Applying an adequate catalyst in a catalytic cracking process at proper reaction conditions has a great potential to lower the required cracking temperature, to shorten the cracking time, to increase the cracking ability of plastics, and to narrow the product distribution. Thus, the depolymerization of PET process could be a more efficient and economical way to recycle waste PET products than the noncatalytic process.

1. From the result, dibutyltin oxide is the most active catalyst among others in the depolymerization of PET reaction. Thus, the process of the depolymerization of PET with a dibutyltin oxide catalyst has a potential to be enlarged to a commercial scale. Pure PET could be rapidly and almost completely decomposed to its DMT's monomer under catalytic cracking. The selectivity of DMT had been improved when the reaction time and the reaction temperature had increased. The reaction was performed well in rather low temperatures (170-180 ^{0}C) with the reaction time of 15-20 minutes. The optimal catalyst-to-PET weight ratio was 0.8 % which yielded 97% of DMT.

2. Due to the effect of the added catalysts that promotes the reaction opportunity to the reactants, the activation energy was decreased in the reaction of depolymerization of PET using catalysts. As the results of those, the required temperature and time would be decreased. In addition, the catalysts also increased the selectivity to the products. The

kinetic plot had conformed to the first-order reaction at the temperature ranging from 160 ^{0}C to 200 ^{0}C with the average activation energy of 154.05 KJ/mol.

Suggestions for future work

Depolymerization of PET by using catalyst should be further studied as follows:

1. Depolymerization of PET should be investigated for other catalysts.
2. The process of the depolymerization of PET using dibutyltin oxide as a catalyst has a potential to be enlarged to a commercial scale.

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APPENDICES

APPENDIX I

TableA-I The effect of time on yield of DMT(%) in depolymerization of PET by using dibutyltin oxide.

Time(min)	Percentage of DMT yield			
	160 ^{0}C	170 ^{0}C	180 ^{0}C	190 ^{0}C
5 min	0	24.72	41.97	80.15
10 min	0	51.12	78.54	91.38
15 min	21.25	82.72	97.56	97.49
20 min	36.56	82.94	97.26	96.81
25 min	45.46	90.92	96.23	97.38
30 min	59.34	92.12	96.56	96.14
35 min	63.13	92.74	97.45	97.04
40 min	62.15	92.74	97.56	96.56

TableA-II The effect of time on yield of DMT(%) in depolymerization of PET by using Cu(II)chloride catalyst.

Time(min)	Percentage of DMT yield				
	$170\ ^0C$	$180\ ^0C$	$190\ ^0C$	$200\ ^0C$	$210\ ^0C$
5	0	0	27.87	40.03	61.39
10	0	5.89	37.87	60.12	88.86
15	4.21	36.48	55.64	88.78	97.06
20	15.3	61.00	76.22	98.67	98.56
25	24	75.51	95.64	97.67	97.67
30	32.13	96.82	98.12	98.55	97.33
35	34.34	98.12	98.43	97.67	97.57
40	34.13	97.45	97.87	97.25	98.12

TableA-III The effect of time on yield of DMT(%) in depolymerization of PET by using Zinc acetate catalyst.

Time(min)	Percentage of DMT yield				
	170 ^{0}C	180 ^{0}C	190 ^{0}C	200 ^{0}C	210 ^{0}C
5	0	6.26	37.59	57.36	62.63
10	0	39.9	67.34	79.23	89.93
15	5.3	65.23	89.71	92.35	97.54
20	23.12	84.5	97.74	97.56	97.12
25	35.75	96.1	97.45	95.25	98.45
30	45.22	96.21	96.12	96.21	98.23
35	48.23	96.23	95.45	97.91	97.43
40	47.43	97.12	97.37	98.03	97.35

APPENDIX II

Properties of Material

Copper (II) chloride 2-water

- **Formula as commonly written:** $CuCl_2.2H_2O$
- **Hill system formula:** $Cl_2Cu_1H_4O_2$
- **CAS registry number:** [10125-13-0]
- **Formula weight:** 170.482
- **Class:** chloride aquo

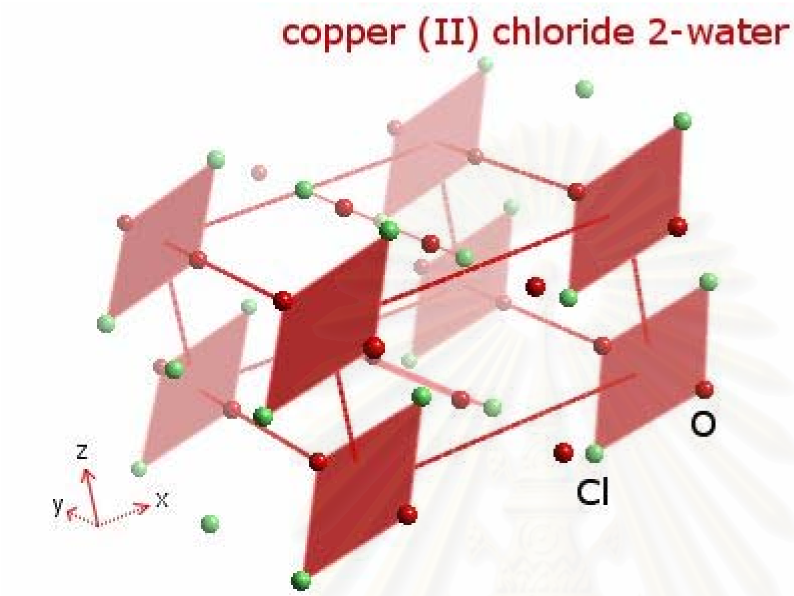
Synonyms

- copper (II) chloride 2-water
- copper chloride 2-water
- copper dichloride 2-water
- cupric chloride

Physical properties

- **Colour:** green-blue
- **Appearance:** crystalline solid
- **Melting point:** 70°C (dehydrates)
- **Boiling point: -**

- **Density:** 2510 kg m^{-3}



Element analysis and oxidation numbers

For each compound, and where possible, a formal oxidation number for each element is given, but the usefulness of this number is limited, especially so for *p*-block elements in particular. Based upon that oxidation number, an electronic configuration is also given but note that for more exotic compounds you should view this as a guide only.

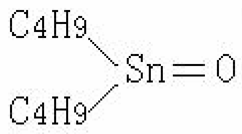
Element	%	Formal oxidation state	Formal electronic configuration
Cl	41.59	-1	[Ne].3s^2.3p^6
Cu	37.27	2	[Ar].3d^9
H	2.36	1	1s^0
O	18.77	-2	[He].2s^2.2p^6

Zinc acetate $(C_4H_6O_4Zn{\bullet}2H2O)$

Physical and Chemical Properties

Appearance:	White crystals or powder.
Odor:	Slight acetic acid (vinegar) odor.
Solubility:	43g in 100g water.
Density:	1.74
pH:	No information found.
% Volatiles by volume @ 21 ^{0}C (70 ^{0}F):	0
Boiling Point:	Decomposes.
Melting Point:	237 ^{0}C (459 ^{0}F)
Vapor Density (Air=1):	No information found.
Vapor Pressure (mm Hg):	No information found.
Evaporation Rate (BuAc=1):	No information found.

Dibutyltin oxide



Physical and chemical proprieties:

$(C_4H_9)_2$ Sn0

White Powder

Molecular Weight 248.92

Density 1.58 g/mL

% Sn 47.68 %

M.P. > 300°C

1.General Information

Name:	Dibutyltin Oxide
Trade Name:	DBTO
Chemical Name (If Single Substance):	Di-n-butyl-oxo-stannane
Chemical Family:	Organotin Compound
Formula:	(n-C4H9)2SnO

2. Ingredients and Physical Data

Identity:	dibutyltin oxide
CAS #:	818-08-6
%	>90
TLV	0.1 mg/ml as Sn
Boiling Point	N/A
Freezing Point:	N/A
Specific Gravity (H2O=1):	1.58
Vapor Pressure:	N/A
Vapor Density:	N/A
Solubility in Water:	Slight
% Volatiles:	0.3% (moisture)
Evaporation Rate:	N/A
Molecular Weight:	248.92
Appearance and Odor:	White powder characteristic odor

APPENDIX III

- Calculation of the percentage yield of DMT from HPLC analysis

Table A-IV **Area of the percentage yield of DMT standard**

%DMT std.	Area
20	105312
40	178723
60	278210
80	359752
100	490896

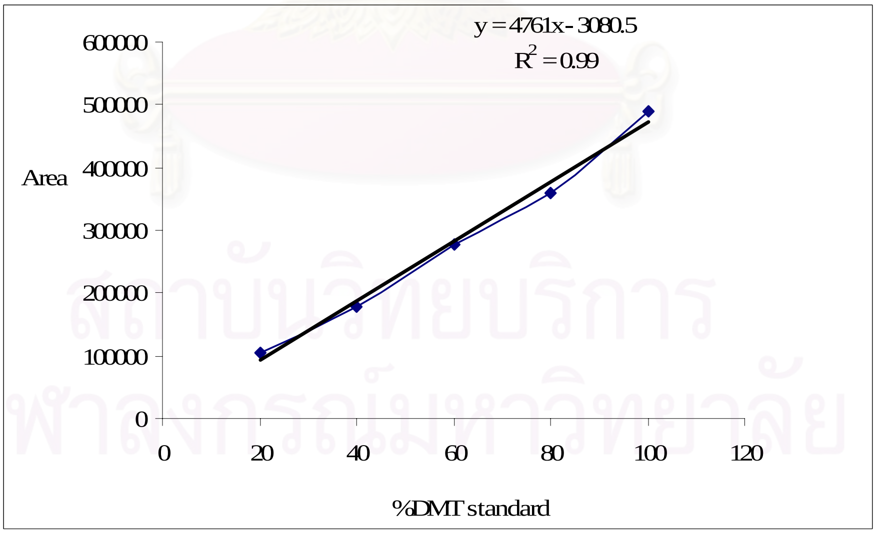


Figure A The relationship between %DMT standard and area in HPLC

Table A-V Calculation of the percentage yield of DMT from HPLC analysis

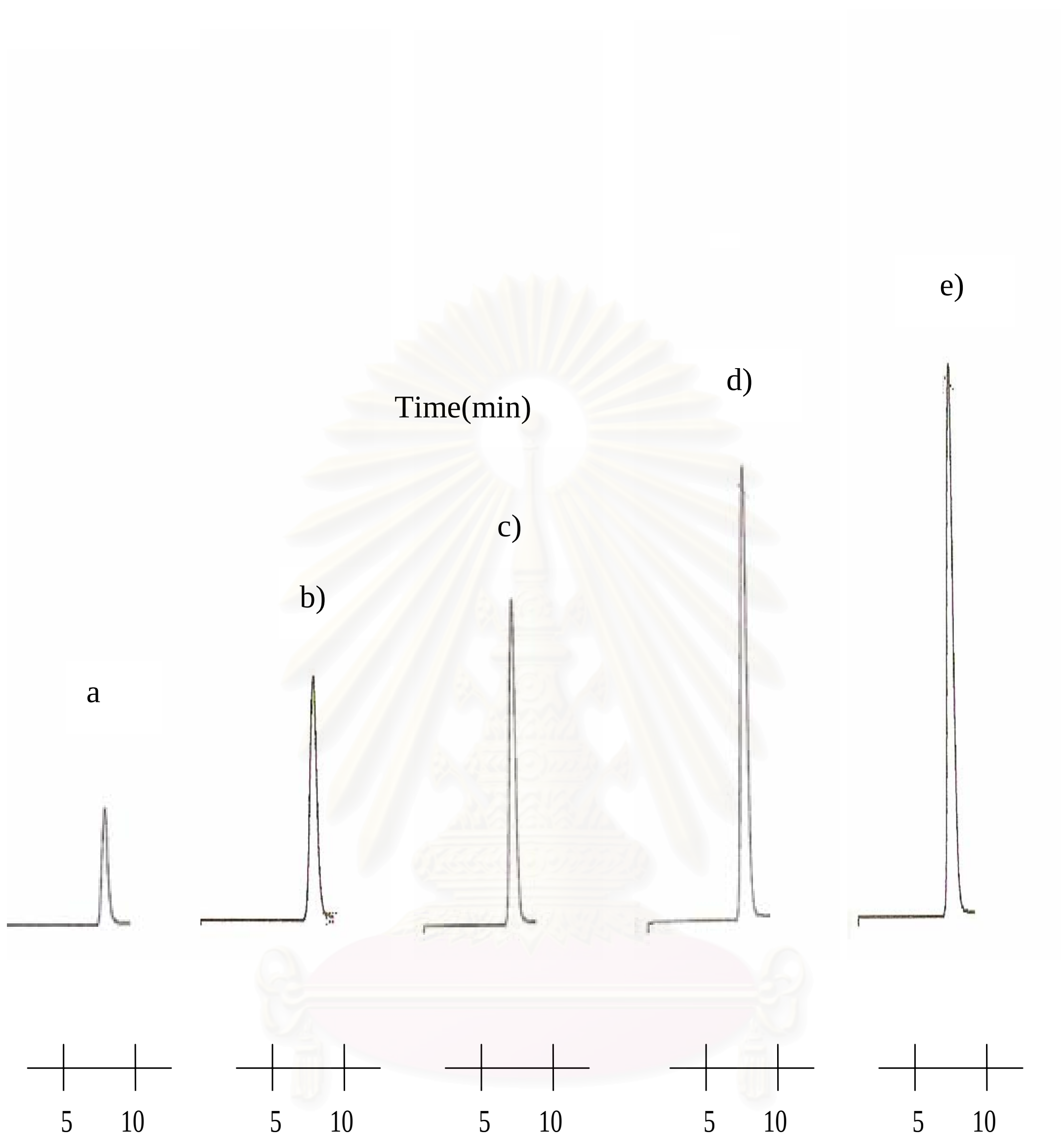
Run No.	Condition (temp, time, %catalyst)	Y(area)	X(%yield of DMT)
DC1	180,30,0.3	308384	65.42
DC2	0.5	387794	82.10
DC3	0.8	457360	96.71
ZC1	200,30,0.3	376238	79.67
ZC2	0.5	454255	96.06
ZC3	0.8	407821	86.31
CC1	200,30,0.3	388272	82.20
CC2	0.5	402975	85.29
CC3	0.8	406475	86.02

Example from the equation of figure A:

X = DC1 (%yield of DMT) = (Y + 3080.5)/4761

= (308384+ 3080.5)/4761

= 65.42



FigureA-I Standard of DMT at a) 20% DMT b)40% DMT c) 60%DMT d)80%DMT e) 100%DMT

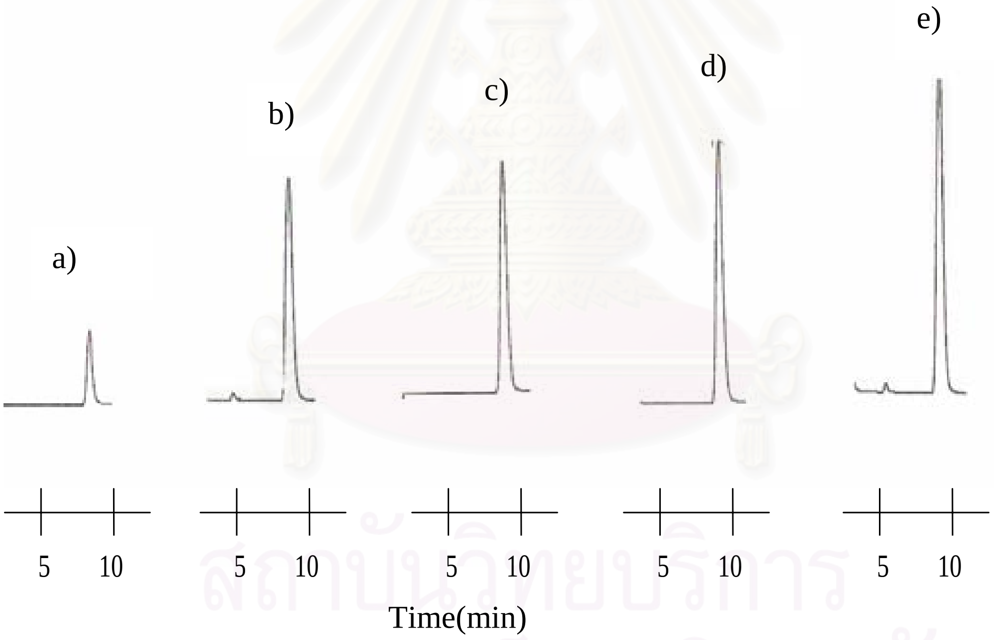


Figure A-II The result samples of HPLC of DMT (effect of time to depolymerization of PET by using dibutyltin oxide catalyst at 160 ^{0}C, a)15 min, b) 20 min, c) 25 min, d)30 min, e) 35 min

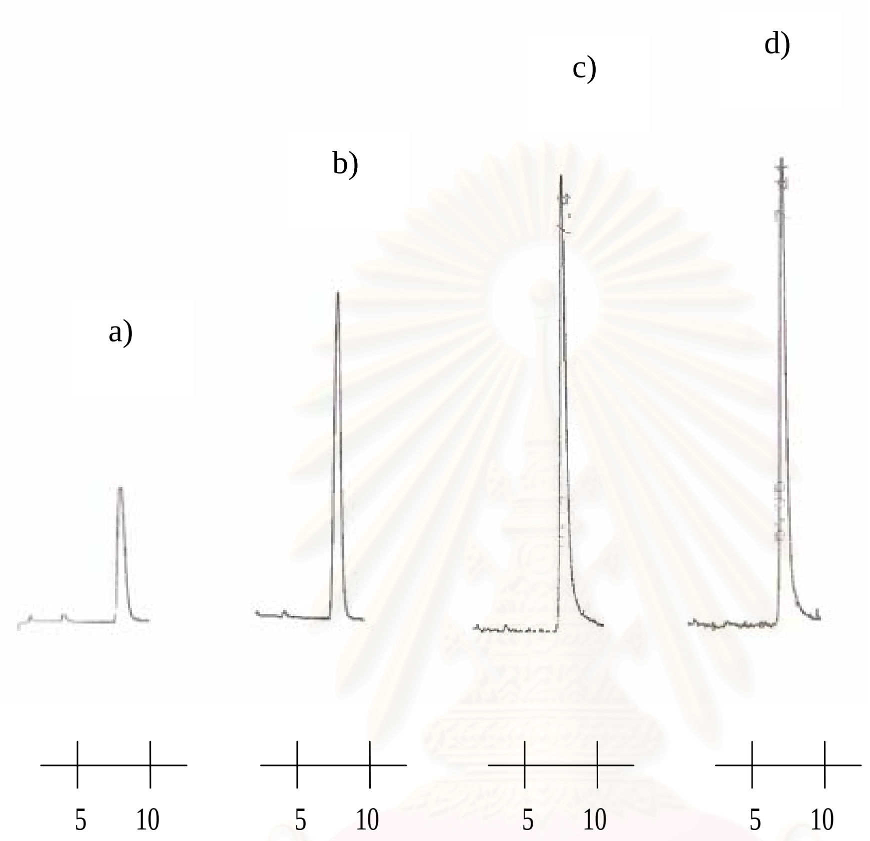


Figure A-IV The result sample of HPLC of DMT (effect of time to depolymerization of PET by using dibutyltin oxide catalyst at 180 ^{0}C, a) 5 min, b) 10 min, c)15 min, d) 20 min,

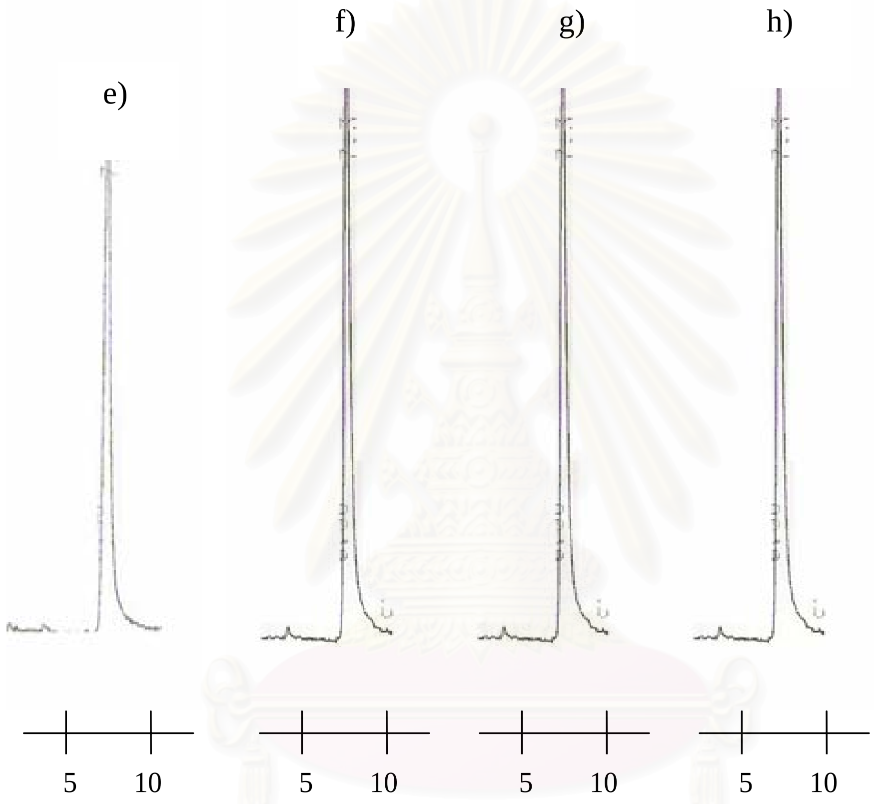


Figure A-V (continue) The result samples of HPLC of DMT (effect of time to depolymerization of PET by using dibutyltin oxide catalyst at 180 ^{0}C, e) 25 min, f)30 min, g) 35 min, h) 40 min

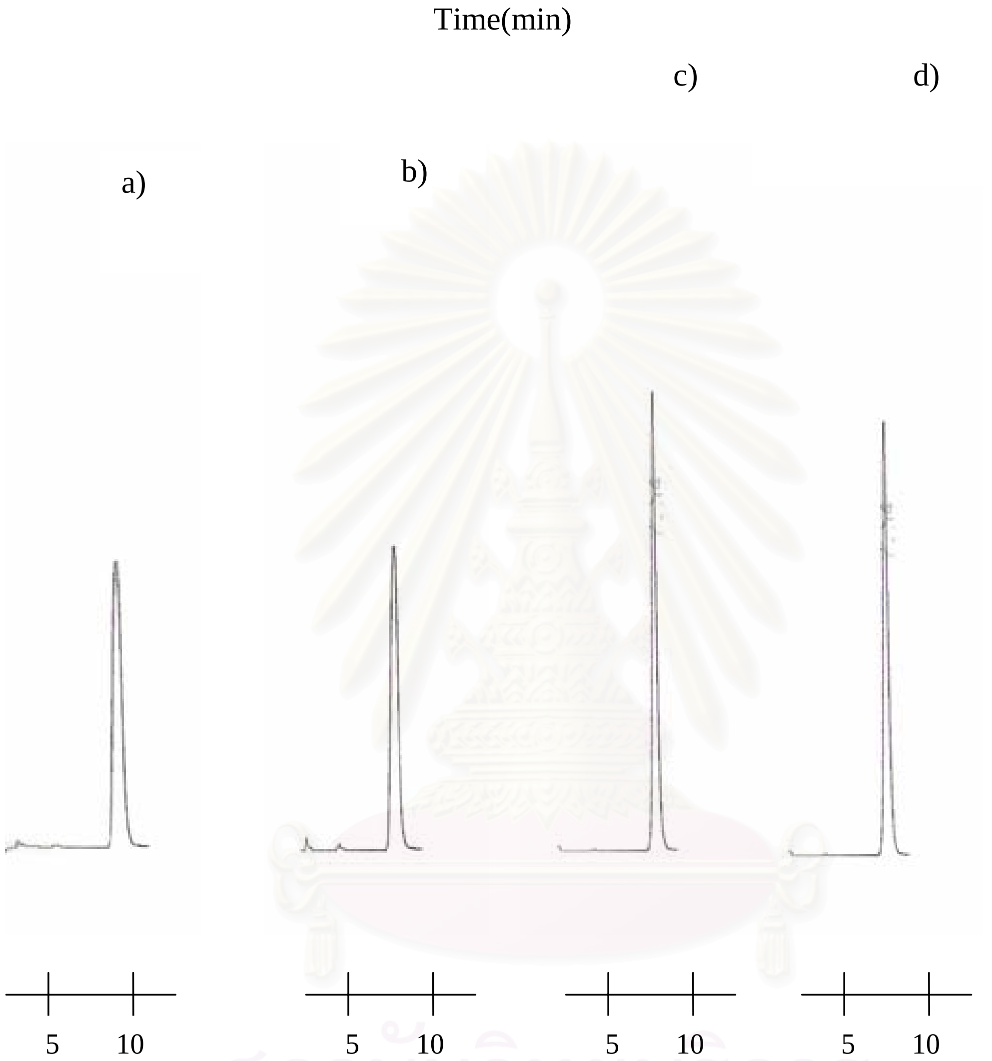
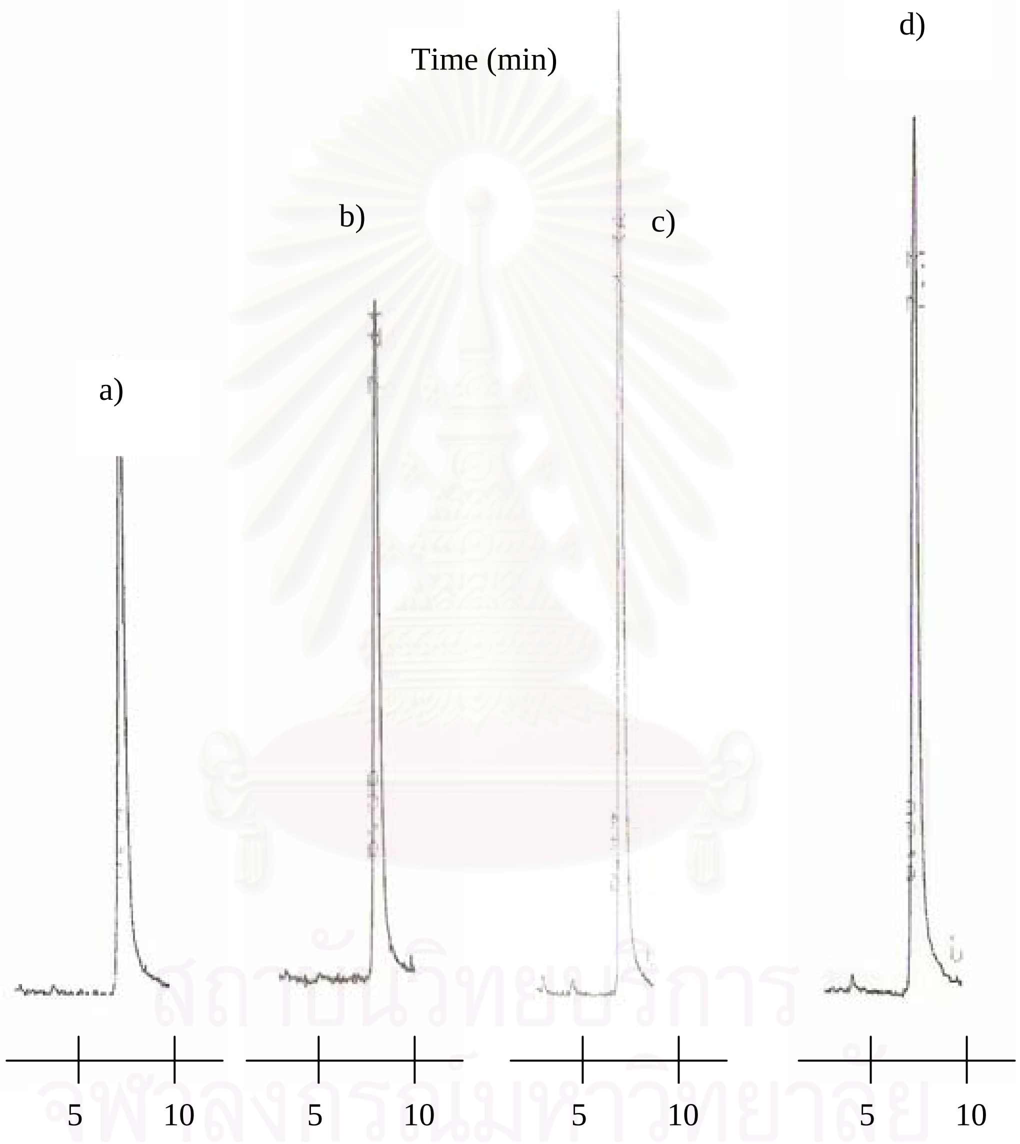
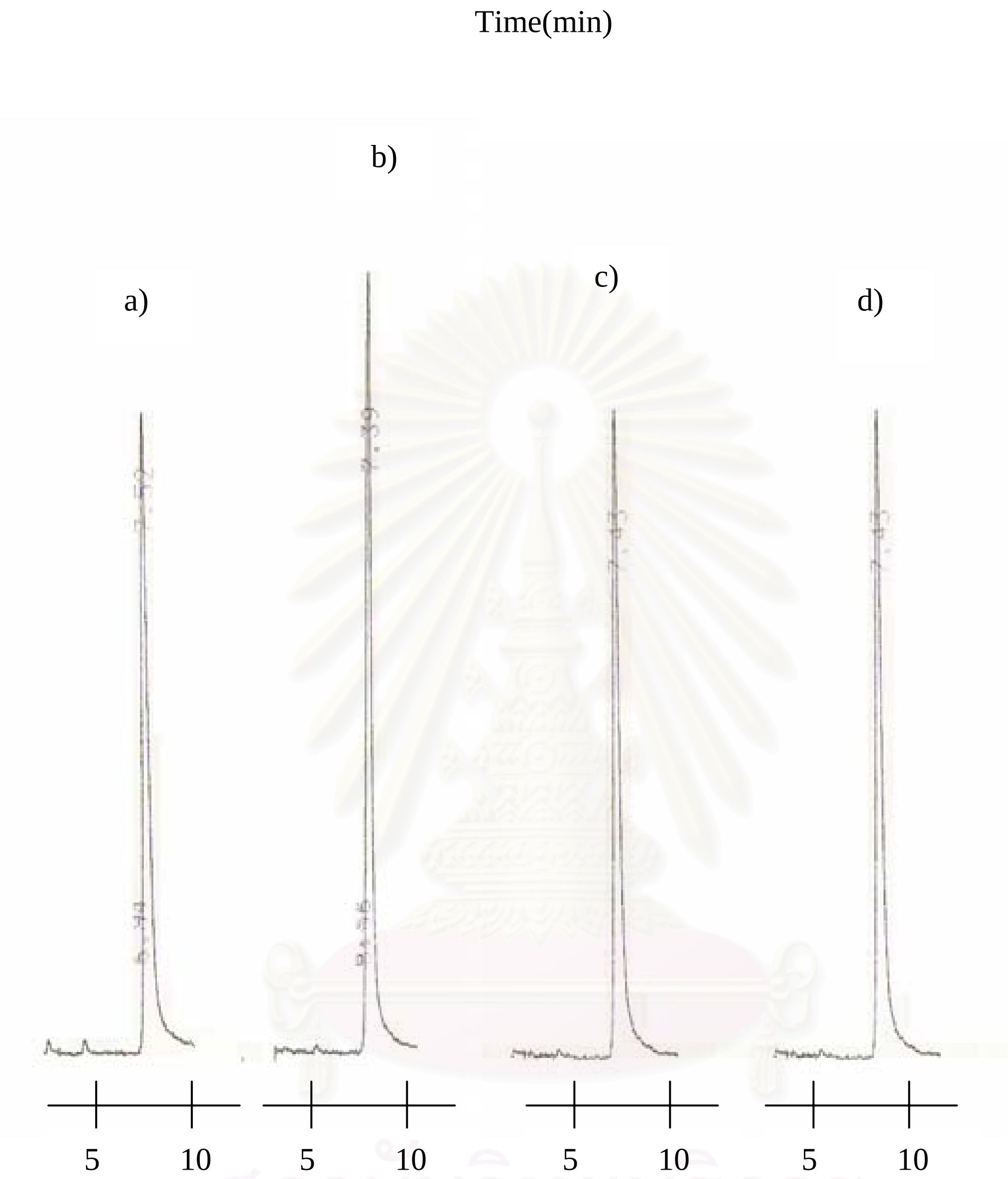


Figure A-V (continue) The result sample of HPLC of DMT (effect of time to depolymerization of PET by using dibutyltin oxide catalyst at 190 ^{0}C, a) 5 min, b)10 min, c) 15 min, d) 20 min



FigureA-VI The result sample of HPLC of DMT (effect of catalyst-to-PET to depolymerization of PET by using dibutyltin oxide catalyst at 180 ^{0}C, 30min

a) 0.3%, b) 0.5%, c) 0.8%, d) 1%



FigureA-VII The result sample of HPLC of DMT (effect of catalyst-to-PET to depolymerization of PET by using Zinc acetate catalyst at 200 ^{0}C, 30min

a) 0.3%, b) 0.5%, c) 0.8%, d) 1%

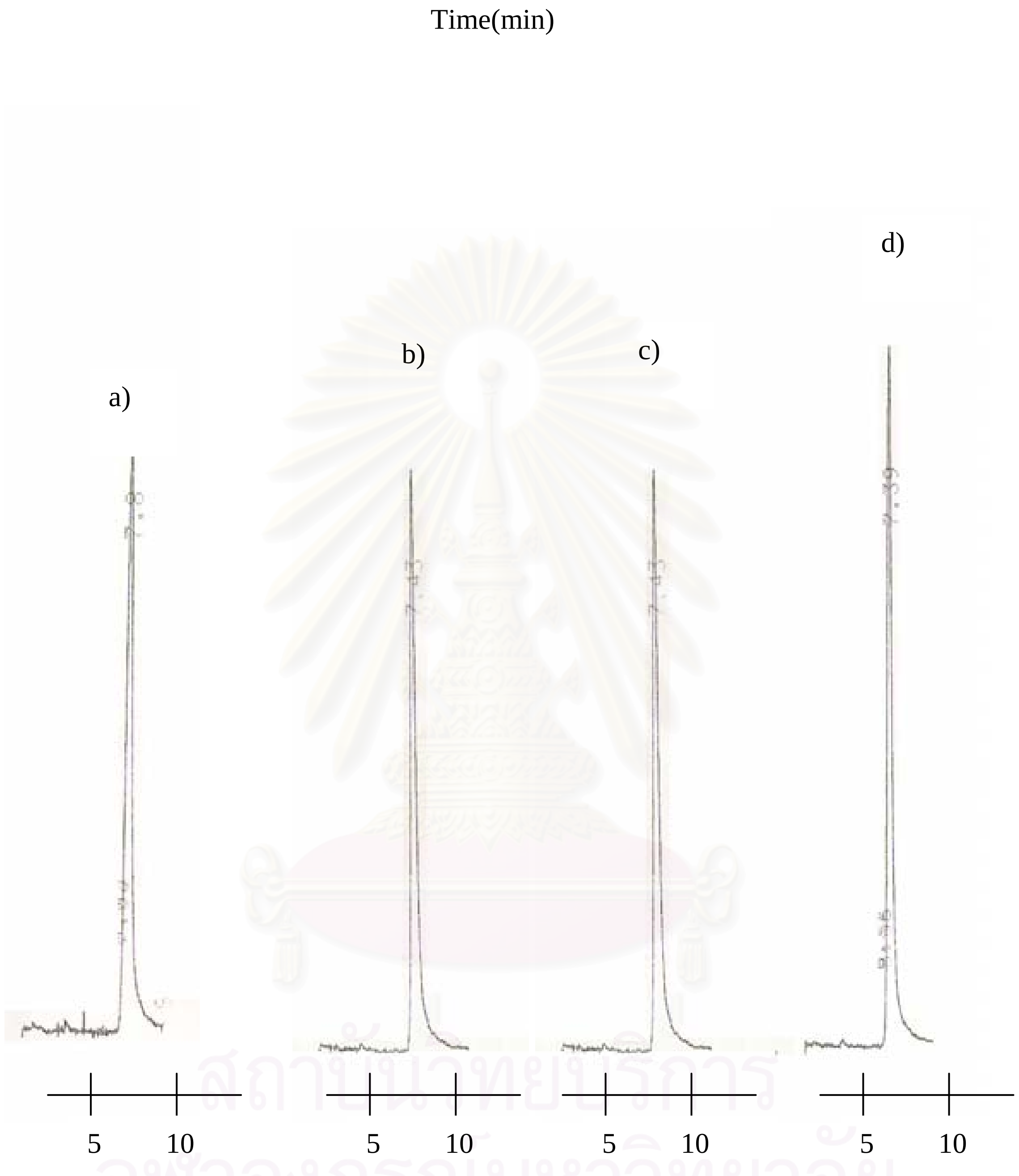


Figure A-VIII The result sample of HPLC of DMT (effect of catalyst-to-PET to depolymerization of PET by using Cu(II)chloride catalyst at 200 ^{0}C, 30min

a) 0.3%, b) 0.5%, c) 0.8%, d) 1%

BIOGRAPHY

Miss Naruephat Tangmankongworakoon was born on August 13, 1974 in Nakornsawan; She received a Bachelor's degree of Science in Chemical Industry, Faculty of Science at Chiangmai University in 1996 and Master's degree of Science in Chemical Technology, Faculty of Science, Chulalongkorn University in 2000. Since 2001, she has studied for Doctoral degree in Chemical Technology at the Faculty of Science, Chulalongkorn University.