CHAPTER I

INTRODUCTION

1.1. Polyester

An ester is a compound whose structure may be derived by the replacement of the acidic hydrogen of an acid with an alkyl, aryl, alicyclic or heterocyclic group [4].

Polyester are defined as polymers containing recuring -CO-O- groups in the main chain. Polyester can be produced by [2]:

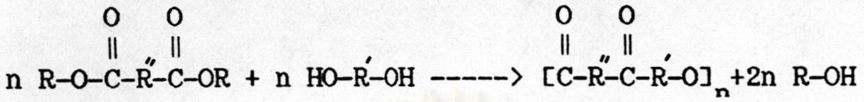
a) Direct esterification of a diacid with a diol

$$n\ HO\text{-}R\text{-}OH + nHO_2C\text{-}R'\text{-}CO_2H \text{ -----> } HO(R\text{-}OCO\text{-}R'\text{-}COO)_n + (2n-1)H_2O$$

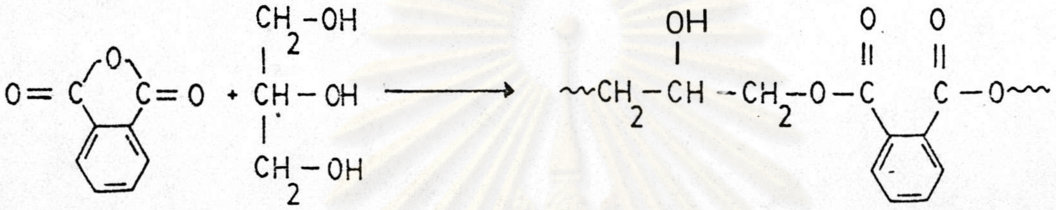
b) The self-condensation of an w-hydroxy carboxylic acid

$$n\ HO\text{-}R\text{-}CO_2H \text{ -----> } H(O\text{-}R\text{-}CO)_nOH + (n-1)H_2O$$

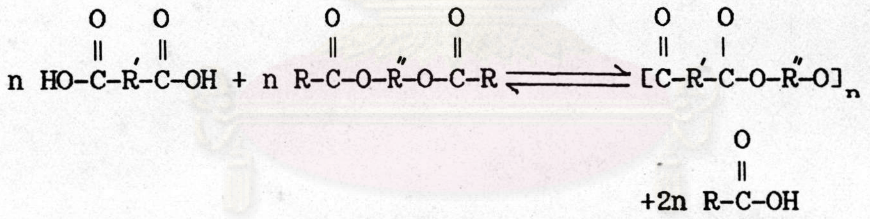
c) Ester Interchange of an aliphatic or aromatic diester of diacid with a diol



$$n\ R{-}O{-}\overset{\overset{O}{\|}}{C}{-}R''{-}\overset{\overset{O}{\|}}{C}{-}OR + n\ HO{-}R'{-}OH \longrightarrow [\overset{\overset{O}{\|}}{C}{-}R''{-}\overset{\overset{O}{\|}}{C}{-}R'{-}O]_n + 2n\ R{-}OH$$

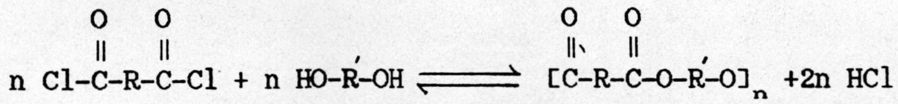


d) Esterification of diacid with a diester or a bisphenol



$$n\ HO{-}\overset{\overset{O}{\|}}{C}{-}R'{-}\overset{\overset{O}{\|}}{C}{-}OH + n\ R{-}\overset{\overset{O}{\|}}{C}{-}O{-}R''{-}O{-}\overset{\overset{O}{\|}}{C}{-}R \rightleftharpoons [\overset{\overset{O}{\|}}{C}{-}R'{-}\overset{\overset{O}{|}}{C}{-}O{-}R''{-}O]_n + 2n\ R{-}\overset{\overset{O}{\|}}{C}{-}OH$$

e) Esterification of diacid chloride with a glycol or bisphenol



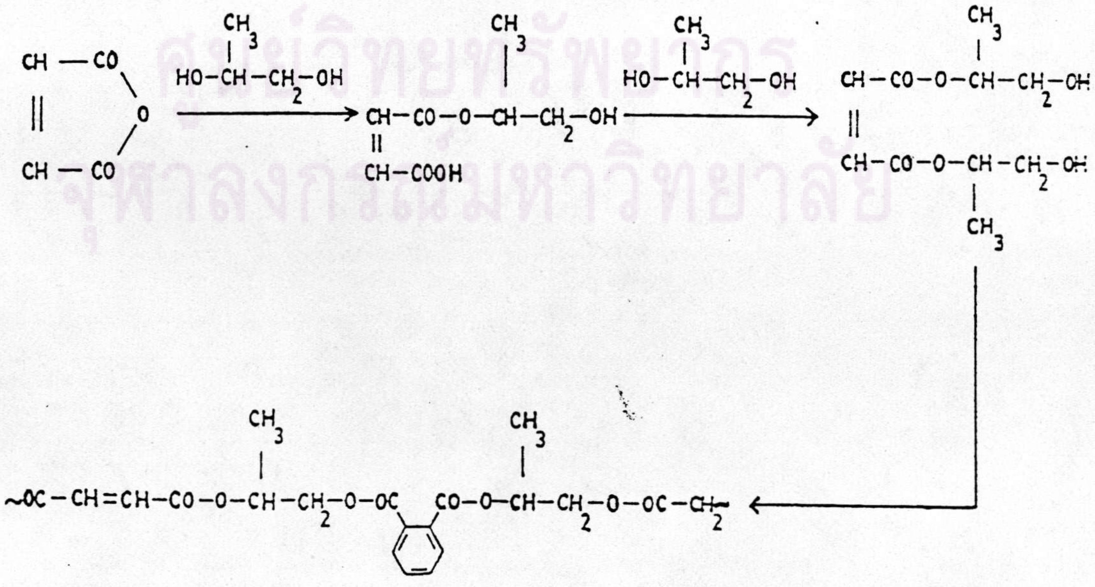
$$n\ Cl{-}\overset{\overset{O}{\|}}{C}{-}R{-}\overset{\overset{O}{\|}}{C}{-}Cl + n\ HO{-}R'{-}OH \rightleftharpoons [\overset{\overset{O}{\|}}{C}{-}R{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'{-}O]_n + 2n\ HCl$$

Polyesterification is a step polymerization so that it is an equlibrium reaction, the by product (such as water, hydrogen chloride etc.) must be continuously removed to achieve high conversions and high molecular weight. Control of the polymerization temperature is important to prevent undesirable side reactions such as dehydration of diol an ester pyrolysis which are produced by high temperature reaction [1].

Polyester are conveniently classified into the following types [4].

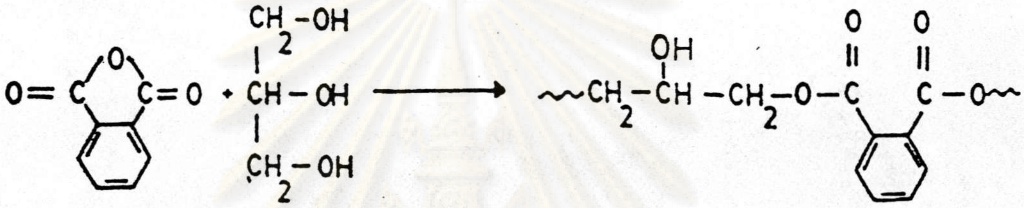
1.1.1. Linear unsaturated polyesters

Linear unsaturated polyester are prepared commercially by the reaction of a saturated diol with a mixture of an unsaturated diacid and a "modifying" diacids or corresponding anhydrides such as



1.1.2. Network polyesters

The principle raw materials involved in the preparation of alkyd resins are polyhydric alcohols (polyols) and diacids or corresponding anhydrides together with the modifying oils.



1.1.3. Linear saturated polyesters

Linear saturated polyesters are prepared by a diol-dicarboxylic acid condensation. Often a monohydric alcohol or a monocarboxylic acid is included in the reactant; in this way, reaction end-groups are eliminated and also the molecular weight of the product may be controlled. Commonly used reactants are given in Table 1.

$$n\ \mathrm{HO{-}R{-}OH} + n\ \mathrm{HO_2C{-}R'{-}CO_2H} \text{ -----> } \mathrm{HO(R{-}OCO{-}R'{-}OCO)_nH} + (2n-1)\mathrm{H_2O}$$

Table 1. Reactants used for the preparation of polyester.

Diol	Dicarboxylic acid	Monohydric alcohols	Monocarboxylic acid
Ethylene glycol	Adipic acid	n-Butanol	Capric acid
Diethylene glycol	Sebacic acid	n-Octanol	Lauric acid
Propylene glycol	Phthalic acid	n-Decanol	Pelargonic acid
Triethylene glycol	Azelaic acid	2-Ethoxylhexanol	Benzoic acid

Polyesterification Catalysts [2]

Most polyesterification reactions, with the principle exception of those based on the reaction of an acid chloride, require catalysis to maintain resonable rates under relatively moderate conditions chosen to prevent side reactions for examples, p^1-toluenesulfonic acid, oxide and acetate of metal ions or sodium alkoxytitarates. It is difficult to classify their activity as being either acidic or basic.

Structure-Melting Point Relationships in linear Polyesters [2]

The melting point of a crystalline polymer is one of the most important property characteristics govering the usefulness of that polymers. Polyesters as a class offer perhaps the best opportunity of all linear, step-growth polymers to study the relationship between melting point and the molecular structure of the polymer repeating unit because more structural type of linear polyesters have been prepared and classified than have any other classes of step-growth polymers.

The melting temperature of a crystalline polymer depends on a number of intermolecular and intramolecular structural characteristics of the repeating unit which are:

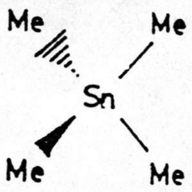
1. structural regularity
2. bond flexibility
3. close-packing ability
4. interchain attraction

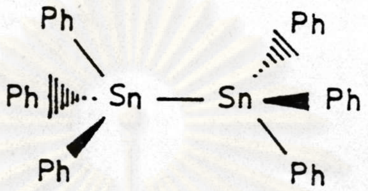
High melting points are generally associated with either highly regular structure, or rigid molecular structures, or a capability of close-packing of polymer chains, or strong interchain attraction or a combination of these factors.

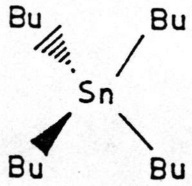
2. Organotin compounds

Organotin compounds are defined as compounds containing at least one tin-carbon bond. Tin is an element in group IV of the Periodic Table so that it has a $5s^2$ $5p^2$ electronic configuration. While organotin (II) is known, organotin (IV) is the most common form; with few exceptions, monomeric stannylenes R_2Sn exist as short-lived intermediates which are readily transform into tin (IV) oligomer $(R_2Sn)_n$ [9].

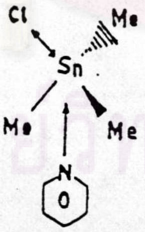
Quadrivalent organotin often presents the tetrahedral sp^3 hybridization. This is so far tetraorganotins, hexaorganoditins, organotin hydrides and most of the thiotin derivatives.

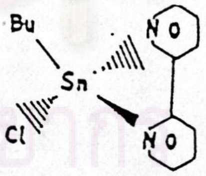


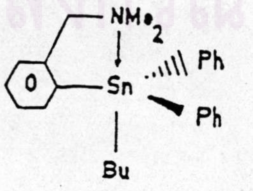


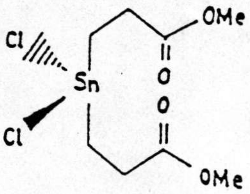


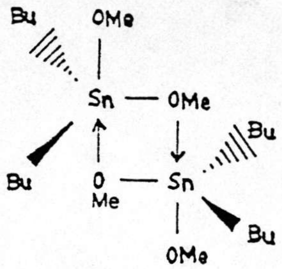
However, when tin bears more electronegative substituents, its lewis acidity increases and coordination with electron-rich sites leads to sp^{3}d^2 (trigonal bipyramid) or sp^{3}d^2 (octahedral) hybridization. Accordingly, acid-base complexs are obtained and the compound may show intramolecular coordination or autoassociation in the solid state or in solution, leading to dimer or polymer:

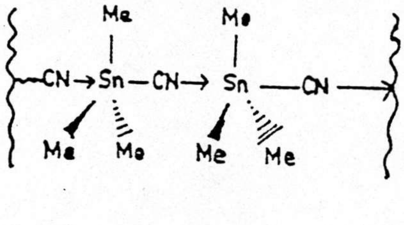




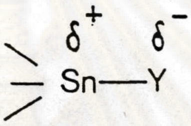








Most organotin compounds of interest for organic synthesis are liquid or solid and soluble in most organic solvents because the covalent radius of tin is 0.14 nm and consequently bond lengths of tin are long; average value in nm are Sn-C 0.22, Sn-H 0.17, Sn-Cl 0.24, Sn-O 0.21, Sn-S 0.24, Sn-Sn 0.28 nm. In spite of the differences in electronegativity the bonds are commonly considered as essentially covalent by easily polarizable.



In Consequence, organotins show little ionization in solution

Industrial synthesis involves obtaining a tetraorganotin compounds, R_4Sn, which is further transformed into organotin chloride, $R_{4-n}SnCl_n$. The chlorides are then efficiently work up into the further, more synthetically useful derivatives [3].

1.2.1 **Organotin Halides**

The organotin halides occupy a key position in the chemistry of organotin compounds. Indeed, they are used as starting materials for the synthesis of many series of other organotin compounds (23).

The synthesis of organotin halides can be carried out by the following routes [3].

1. The Direct Synthesis

By direct synthesis is meant the direct reaction between tin and an alkyl or aryl halide to yield an organotin halide. The simplest reaction would be

$$Sn + 2RX \text{ -----> } R_2SnX_2$$

2. Alkylation and Arylation of Tin halides.

Tin (II) chloride, Tin (IV) chloride and organotin halides can be alkylated or arylated with such reagents as the Grignard reagent, alkyl and aryllithiums, organomercury compounds, trialkyl aluminium, etc. In most instances, however, a mixture is obtained, from which individual organotin halides are seperated with difficulty.

The reaction between Grignard reagent and tin (IV) chloride has been studied for the preparation of organotin halides, according to the reactions.

$RMgX + SnX_4 \text{ -----> } RSnX_3 + MgX_2$

$2RMgX + SnX_4 \text{ -----> } R_2SnX_2 + 2MgX_2$

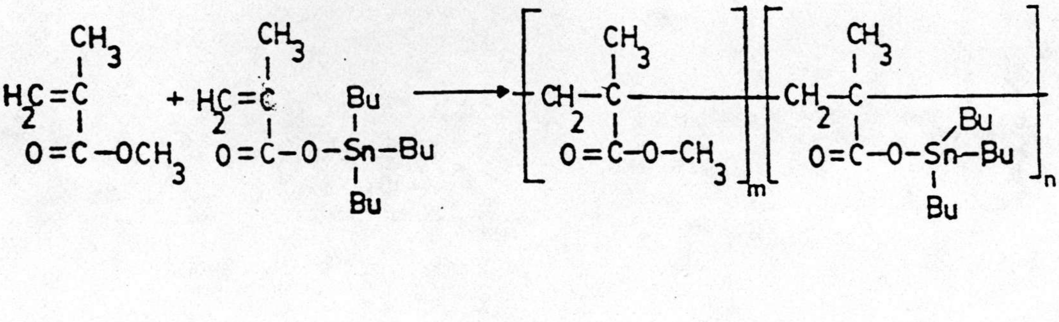
$3RMgX + SnX_4 \text{ -----> } R_3SnX_2 + 3MgX_2$

In the Synthesis of organotin halides the method of Grignard reagent hes been the most widely used.

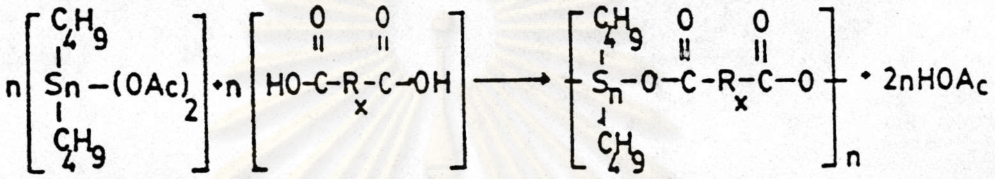
1.2.2 Organotin polymers

Organotin polymers are composed of organotin monomer. Advantageously, organotin polymers are used industrially,

In 1970, C.J. Evans [25] prepared an additive in antifouling paint and coating for the protection of ships and yachts hulls and sea water cooling pipes from the attachment of barnacles, sea grass, hydroids and other marine organisms. In these cases, tributyl (or triphenyl-) tin groups are chemically bound to the polymer backbone, e.g. poly(tributyltin methacrylate/methyl methacrylate) is achieved from copolymerization of tributyltin-methacrylate with methyl methacrylate.



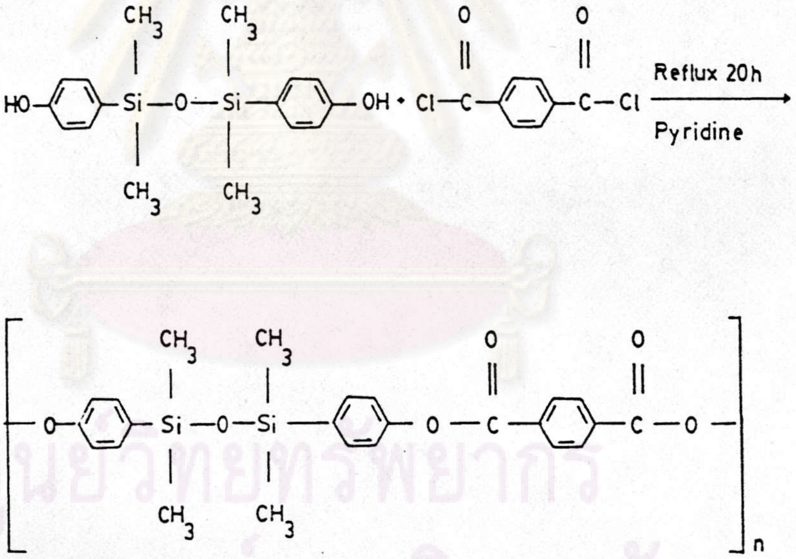
Another application of organotin polymers are used as organomettalic elastomer. In 1958, T.M. Andrews, F.A. Bower, B. R. Laliberte and J. C. Montermoso [15]. prepared dibutyltin dicarboxylic acid esters. The general type is illustrated by the reaction of dibutyltin diacetate and a dicarboxylic acid



$$n\left[\overset{C_4H_9}{\underset{C_4H_9}{Sn}}-(OAc)_2\right]+n\left[HO-\overset{O}{\overset{\|}{C}}-R_x-\overset{O}{\overset{\|}{C}}-OH\right]\longrightarrow\left[-\overset{C_4H_9}{\underset{C_4H_9}{Sn}}-O-\overset{O}{\overset{\|}{C}}-R_x-\overset{O}{\overset{\|}{C}}-O-\right]_n+2nHOAc$$

It is known that dibutyltin acetate and dibutyltin oxide are found to react readily with linear and cyclic dicarboxylic acid to form identical derivatives [15]. Whereas such short chain aliphatic acid such as succinic acid and adipic acid gives soluble cyclic derivatives of low molecular weight, and oxalic acid yields an insoluble, infusible product that has the characteristic salt. The cyclic terphthalic acid anhydride, the long chain sebacic acid, however, give linear polymers. The molecular weights vary from that of dimers to the order of 3000 for the sebacic acid product.

In other organomettallics, for example, organosilicons are used in many applications. Kimohiro Matsukawa and Hiroshi Inoue, [19], synthesized siloxane-containing polymers by incorporation of siloxane chains into polymer backbone which is expected to provide specific characteristics such as heat resistance, surface properties, gas permeability, chain flexibility, oxygen plasma resistance and so on. They prepared 1,3 Bis(p-hydroxypheny)disiloxanes to be polymerized with isophthaloyl chloride, terephthalic acid, etc.



The siloxane chains are known to provide thermal stability and chain flexibility to polymer materials. These polymers had thermal properties which were glass temperature (Tg) at 62-79°C, crystalline temperature (Tc) at 160°C and melting temperature at 260°C which were measured by DSC.

1.3. Application of organotin compounds

Organotin compounds have found applications in several area and hence are made industrially on a large scale. The first application of organotin compounds has been in the stabilization of polyvinyl chloride (PVC) to prevent thermal degradation during processing and long-term photodegradation. Dialkyltin derivatives are the additive of choice for the propose, mainly dibutyltin bis(isooctylthioglycolate) in addition to variable amount of butyltin tri(isooctylthioglycolate). The less toxic dioctyltin compounds are used in PVC for food packaging.

Dibutyltin dilaurate is also widely employed as a catalyst for the production of polyurethane foams or for the room temperature curing for silicone rubber.

The biocide properties of triorganotin derivatives are used in area like textile, wood or paint protection, antifouling paint and pesticide or insecticides in agriculture. Triorganotin compounds are most popular, but triphenyl-or-tricyclohexyltin derivatives are also in used while other organotins have more limited applications.

1.4. Objectives

The objectives of the present studies are the investigation of organotin polyesters which comprised of reaction of the organotin dichloride monomer with the dicarboxylic acid. The resulting polymers are then characterized by various means.