# CHAPTER I

## INTRODUCTION

Numerous living organism in sea water including bacteria, algae, other plants as well as marine animals such as molluses, crustaceans etc., attach readily to immersed surfaces causing marine fouling. The major result of this marine fouling in the case of ships is a roughening of the hull which increases ship frictional resistance, so that increased fuel consumption is needed to maintain speed. This increased fuel consumption consequently results in a decrease in the operational range of the ship. Some fouling organisms also may cause physical damage or accelerate corrosion. Excessive fouling may also inhibit the operation of delicate underwater equipment of a scientific nature such as ship mounted sonar equipment which may suffer range loss, signal distortion and increased background noise levels due to the presence of hard shelled macro organisms on the equipment housings. There are also the costs involved in cleaning and repainting, as well as the loss in revenue due to the time spent in dry-dock particularly for the giant ocean-going supertankers. The nature and severity of the fouling community are influenced by a number of factors, including the geographical location, water temperature depth and salinity.

The most practical way of dealing with these fouling problems is to apply an antifouling coating system containing a suitable

biocide to the ship's hull. The toxicant is, there by, slowly released to the surrounding water, thus preventing the attachment of marine organism. An effective antifouling coating contains a toxic agent which is active against a wide range of fouling species at low concentrations, is safe to apply to a vessel and will not pose any long-term pollution problems. The protection afforded must be long-lasting and, in addition, the coating must adhere strongly to the hull without causing any corrosion problems.

## Organotins as Antifoulants

The use of organotin compounds as biocide agents in antifouling paints was suggested in 1943 (1). However, industrial use of such paints started in the sixties, and they are now widely used over the world. Triorganotin compounds have high biocidal activity compared to the analogous mono-, di- and tetra-organotin derivatives. Tributyl- and triphenyl- tin compounds are preferred for use in antifouling systems, on account of their effectiveness against a wide range of marine fouling organisms and their relatively low toxicity to humans. The antifouling activity of triorganotin compounds, $R_3 SnX$, compared to that of other biocides is shown in Table 1.1

The organotin biocides have the advantage that when released into the seawater, they rapidly degrade to non-toxic residues after exerting their antifouling action. The mode of toxic action of triorganotin compounds towards marine fouling organisms is not completely understood. However, it is probably that they are able to depress general metabolism in the cells of these organisms via the inhibition of the vital process of oxidative phosphorylation. For example, studies on vegetative Enteromorpha intestinalis demonstrated

that triphenyltin chloride acts as an energy-transfer inhibitor _in_ _vivo_ for both respiration and photosynthesis.

| Table 1.1 | Comparison of marine biocidal activities of common antifoulants [2],[3] | | |
|-----------|-----------|--------|-----------|
| Compound | Range of activity (p.p.m.) | | |
| | Algae | | Barnacles |
| $R_3SnX$ | 0.01-5 | | 0.1-1 |
| $Cu_2O$ | 1-50 | | 1-10 |
| $R_3PbX$ | 0.1-1 | | 0.1-1 |
| RHgX | 0.1-1 | | 0.1-1 |

## 1. Antifouling Coatings Containing Organotins

### 1.1 Conventional Paint Systems

Prior to the 1960's, conventional antifouling paint systems were largely based on copper (1) oxide as the toxicant [4]. However, following the discovery of the pronounced biocidal activity of the triorganotin compounds, a number of organisations conducted raft trials on formulations containing these compounds. By the 1960's, organotins had achieved commercialisation, initially as co-toxicants in high-performance copper paints, gradually came to be used in all-organotin systems. They offered a wide scope of formulating approaches with respect to pigments and binders, and they did not contribute to corrosion on steel or aluminum, which can be a problem

with copper oxide paints.(5) The preferred tributyltin derivatives are the bis(tributyltin) oxide (TBTO) and tributyltin fluoride (TBTF). The former compound is miscible with paint solvents and is readily incorporated into most antifouling coatings. It's plasticising action on the paint film restricts the amount that can be added to a typical vinyl system to approximately 13% by wt. or 20% by vol.(dry film) (6). In contrast, tributyltin fluoride is a solid which is insoluble in common paint solvents and behave as an inert pigment. Typical formulations are shown in Table 1.2 and Table 1.3 TBTF has also been used as a cotoxicant in commercial cuprous oxide formulations. More recently, commercial systems incorporating triphenyltin compounds as the sole toxicant, typically in vinyl or chlorinated rubber binders, have become available.

The effectiveness of these antifouling coatings depends on the controlled release of the triorganotin biocide. A paint system will perform satisfactority if a balance can be maintained between a flux of toxicant sufficient to provide an effective antifouling action and a leaching rate which does not deplete the reservoir of toxicant in a short period of time. The factors reported to influence leaching of organotin antifoulants are summarised in Table 1.4

| Table 1.2 | Vinyl rosin marine antifouling paint |
|---|---|
| | Parts/wt. |
| Red Iron Oxide | 15.12 |
| Talc | 11.22 |
| Zinc Oxid | 7.08 |
| VAGH[a] | 11.16 |
| Rosin | 3.73 |
| Methyl Isobutyl Ketone | 20.31 |
| Xylene | 18.84 |
| Bentone 27 } Prewet | 0.51 |
| Methanol 95% } Prewet | 0.17 |
| bioMet TBTF Marine Antifoulant[b] | 11.86 |
| | ------ |
| | 100.00 |

(a) = Union Carbide

(b) = bioMet is a registered trademark of M & F chemicals, Inc.

| Table 1.3 | Chlorinated rubber marine antifouling paint |
|---|---|
| | Parts/wt. |
| Red Iron Oxide | 20.0 |
| Talc | 8.5 |
| Zinc Oxide | 9.4 |
| Bentone 27} Prewet | 0.7 |
| Methanol 95%} Prewet | 0.2 |
| bioMet TBTF Marine Antifoulant | 15.7 |
| Parlon⁽ᵃ⁾ S-20 (50% in Xylene) | 13.8 |
| W W Gum Rosin (60% in Xylene) | 23.0 |
| Xylene | 8.7 |
| | -------- |
| | 100.0 |

(a) = Hercules Incorporated.

These conventional paint systems containing organotin toxicants depend on a leaching mechanism to deliver the biocide to the surface of the paint film. Thus, release of the antifoulant occurs exponentially. Since the mechanism is diffusion controlled, availability of toxicant decrease logarithmically with time as shown in Fig. 1.1 and 1.2
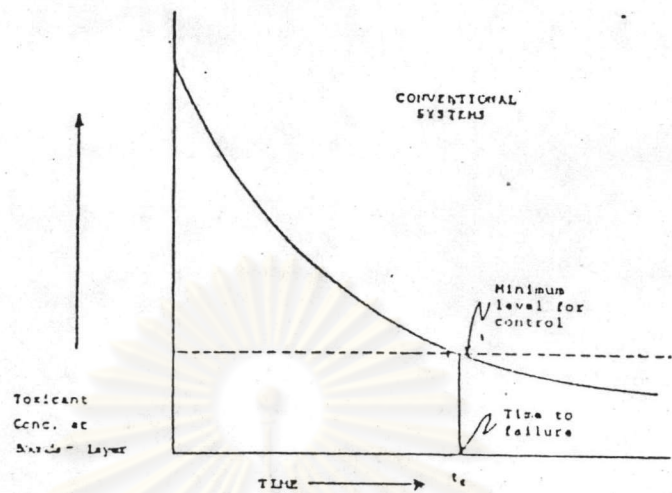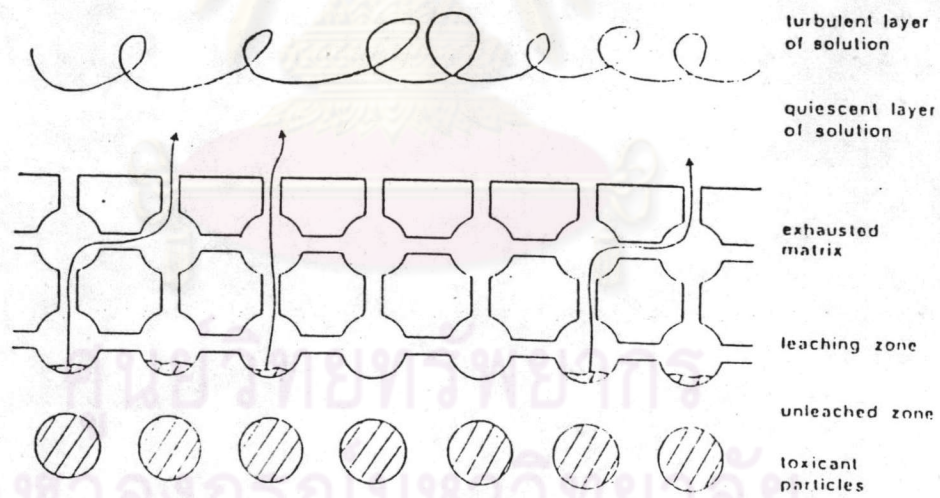
FIG 1.1 --Toxicant release vs. time



FIG 1.2 Diffusion model for leaching of toxicant from a paint film, according to Marson /52/.

| Table 1.4 | Principal factors influencing leaching of organotin antifoulants |
|---|---|

Total percentage solubles

Paint resin / rosin ratio

Level of toxicant

Solubility of toxicant in seawater

Compatibility of toxicant with resin and other film components

Adsorption of toxicant on pigment

Type of resin

Pigment volume concentration

Film thickness

Other additive

## 1.2 Elastomeric System

One of the earliest proprietary systems of this type was based on bis(tributyltin)oxide or sulphide incorporated into chloroprene rubber. Bis(tributyltin)oxide is thought to crosslink the chloroprene and the active agents released upon contact with water are unreacted TBTO, TBTCl etc. resulting from the vulcanising reaction. This system has been demonstrated to be completely effective at preventing fouling over a period of 84 months in tropical water (7) Table 1.5 shows a typical neoprene formula.

| Table 1.5 | Neoprene 351 formulation |
|---|---|

| Ingredient | Formulation (parts by weight) |
|---|---|
| Neoprene WRT | 100.00 |
| FEF Carbon Black | 14.50 |
| PBNA [a] | 2.00 |
| Zinc Oxide | 5.00 |
| Lauric Acid | 3.00 |
| Magnesium Oxide | 4.00 |
| Ethylene Thiourea | 0.75 |
| MBTS [b] | 1.00 |

(a) = Phenyl- $\beta$- naphthylamine.

(b) = Mercaptobenzothiazyl disulphide

Tributyltin fluoride, triphenyltin chloride have been evaluated as well as TBTO in the neoprene formulation shown in Table 1.5 . The slow release mechanism of biocide is considered to involve diffusion-dissolution (8) where by the elastomer remains intact and the toxin is released from the surface on a molecular scale. In general, dissolution of the biocide in water is the rate controlling step.

A novel concept in incorporating organotin compounds into elastomers has been developed and involved the addition of an unsaturated monomer, such as tributyltin acrylate followed by curing with a peroxide. Three reactions are said to occur.

1. cross-linking of the elastomer

2. homopolymerization of the organotin monomer

3. covulcanization of the elastomer and the organotin compound

This process makes it possible to incorporate up to 50 % mass of tributyltin acrylate into different types of elastomer.

### 1.3 Organotin Polymer Systems

A more recent approach designed to increase the performance life of an antifouling coating is the developement of organometallic polymers in which the biocidal moieties are chemically attached to the polymer chain , usually an acrylate polymer. The bioactive group is released on contact with seawater by hydrolysis of the organotin-ester linkage. The depleted outer layer of the paint film, now containing hydrophilic free carboxylate groups , has little integral strength and is easily eroded by moving sea water, exposing a fresh surface layer of organotin acrylate polymer. This hydrolysis and erosion mechanism is continually repeated until no antifouling paint is left on the substrate. The process is illustrated in Fig. 1.3

Thus, while conventional antifouling paints with copper or tributytin additives function by a leaching mechanism, antifoulant paints based on organotin acrylate polymers rely on a controlled hydrolysis and erosion of the paint film to deliver the toxicant. The hydrolysis and erosion mechanism of toxicant release from a properly designed, polymer-based system can result in a constant rate of toxicant release with time .

Thus, in polymer-based systems, the service life of the antifouling coating is a direct linear function of film thickness,

providing the hydrolysis / erosion rate    above    a    minimum   value
necessary  for fouling control.   This is the major differance   between
these systems and conventional systems where the service life is   more
dependent  on factors which affect the diffusion  of toxicant  out  of
the paint film, such as initial toxicant loading and film permeability.
Because  of these intrinsic characteristics, organotin polymers  offer
great versatility to the coating chemist. The adventages for organotin
polymer-based antifouling paints include:

     (1)   Constant toxicant delivery VS. time

     (2)   Erosion rate / toxicant delivery controllable

     (3)   No depleted paint residue to remove and dispose

     (4)   100 % Utilization of toxicant

     (5)   Polishing at high erosion rates

     (6)   Self-cleaning

     (7)   Continuously reactivated

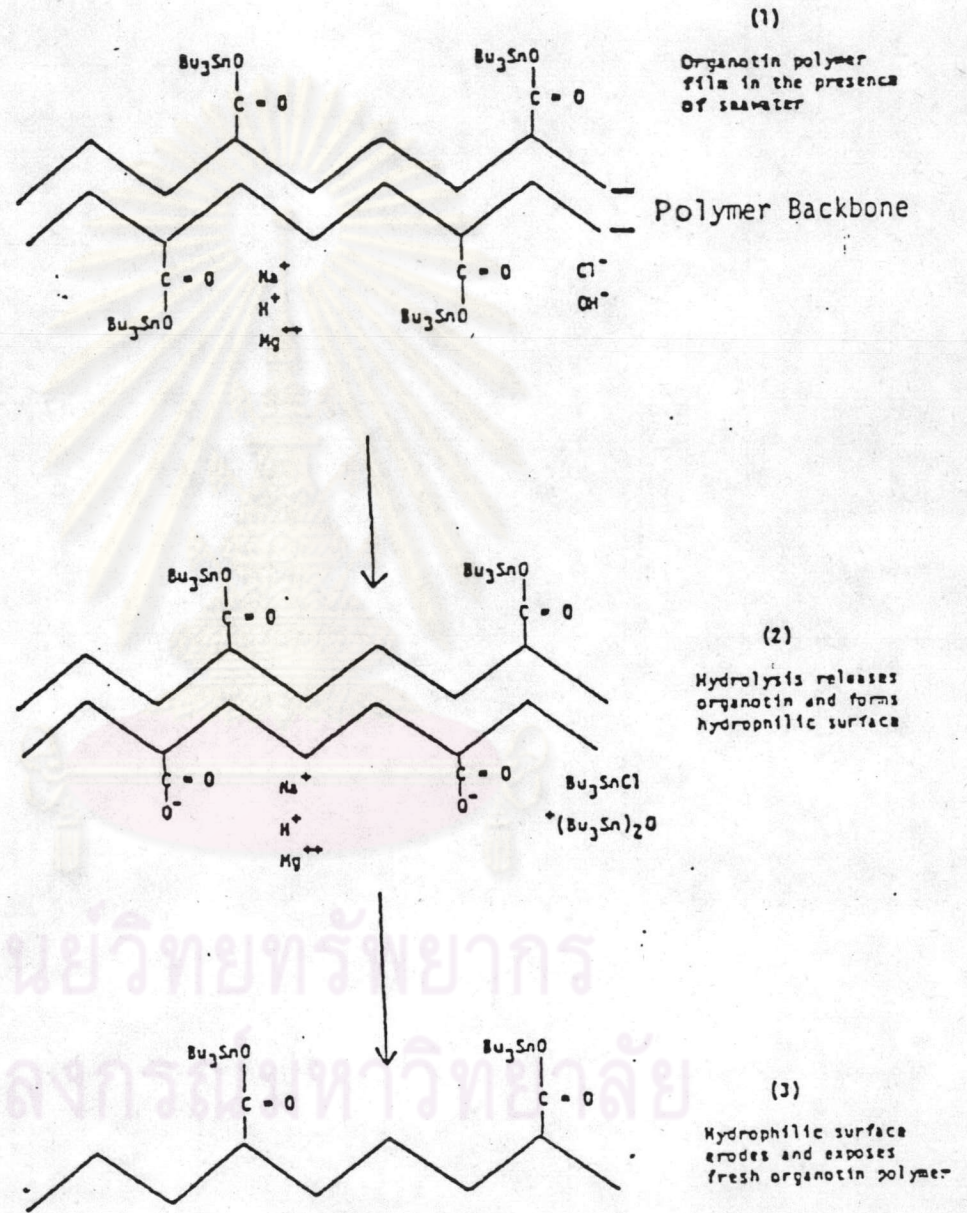FIG 1.3   Mechanism of antifoulant release

### 1.4  Organotin Monomer Synthesis

Three general methods exist for preparing unsaturated organotin monomers. The first method is the reaction of an unsaturated organic salt with an organotin halide as follows:
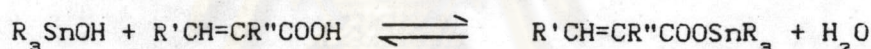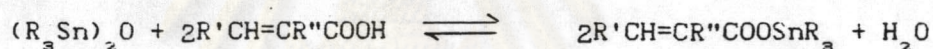
$$(4-n)RCH=CR'COONa + R''nSnX_{(4-n)} \longrightarrow (RCH=CR'COO)_{(4-n)}SnR''_n + (4-n)NaX$$

where $\quad$ n = 0-3

$\qquad$ R, R' = hydrogen , alkyl , aryl

$\qquad\qquad$ R'' = alkyl , aryl

The second method involves the reaction of organotin oxides or hydroxides with unsaturated organic acids.

$$(R_3Sn)_2O + 2R'CH=CR''COOH \rightleftharpoons 2R'CH=CR''COOSnR_3 + H_2O$$

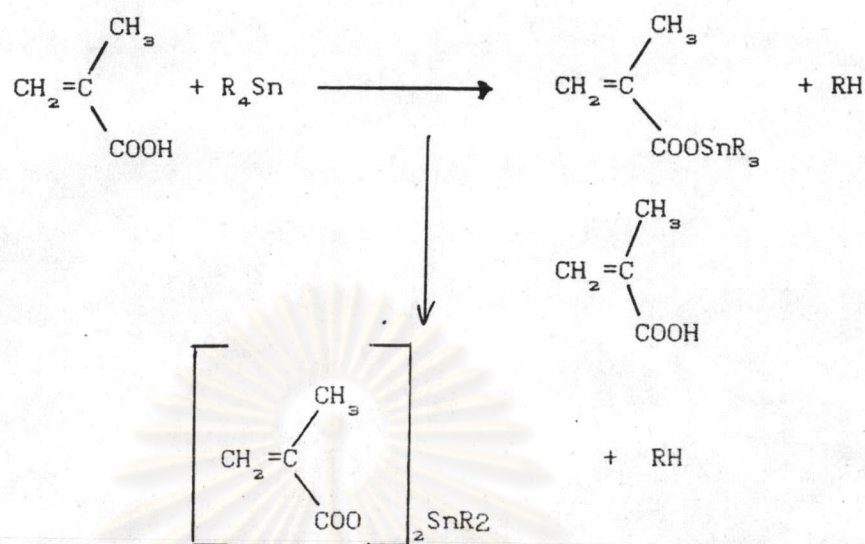$$R_3SnOH + R'CH=CR''COOH \rightleftharpoons R'CH=CR''COOSnR_3 + H_2O$$

The water formed is eliminated with an inert dehydrating agent or collected in the azeotropic distillation head and the equillibrium thus displaced towards salt formation(8). The reaction can be effected at $20^\circ c-50^\circ c$ in absence of hydrocarbon solvents. However, the second process is the most widely used, giving generally good yeilds. Thus acrylate, methacrylates, maleates of tripropyl, tributyl, triphenyltin have been prepared.

The third method uses the reaction of tetraorganic tin derivatives with unsaturated acids, but di-carboxylic acid derivatives are most often produced.

All these three methods, particularly the second one have been used to synthesis different carboxylated tin derivatives (9).

$$CH_2=C\overset{CH_3}{\underset{COOH}{|}} + R_4Sn \longrightarrow CH_2=C\overset{CH_3}{\underset{COOSnR_3}{|}} + RH$$

$$CH_2=C\overset{CH_3}{\underset{COOH}{|}}$$

$$+ RH$$

$$\left[ CH_2=C\overset{CH_3}{\underset{COO}{|}} \right]_2 SnR2$$

## 1.5 Synthesis of Organotin Polymers and Copolymers

There are two main types of organotin polymers , one of which having tin atoms in the backbone which can be synthesized by condensation reactions. The other, having organotin groups in the side chain which can be prepared by free radical polymerization (9). This research project relates to the later type of polymers.

### 1.5.1 Organotin Groups in Polymer Backbone

Polymers having tin atoms in the backbone can be obtained by condensation of difunctional organotin derivatives with other difunctional organic compounds (10), for example, organotin polyesters are obtained by reacting dialkyltin dihalide with disodium salt of a diacid.

$$n\ R_2SnCl_2 + n\ R'(COONa)_2 \longrightarrow -[-SnR_2OOCR'COO-]-_n + 2n\ NaCl$$
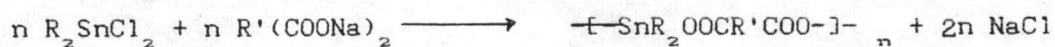
Where R ,R' = hydrocarbon radicals

Thus, acid salts derived from adipic, sebacic, terephthalic may be cited as typical starting monomers. Reaction conditions are not critical for these polymerization.

The condensation products of a bisphenol with a mixture of a diorganotin dihalide and a dicarboxylic acid halide are linear polymers with statistical distribution of organotin groups in the main polymer chain .

The compositions of these polymers are not well understood and can be represented as follows:
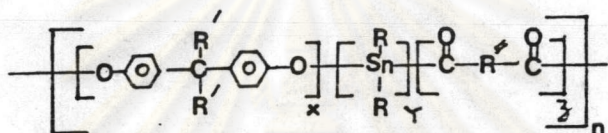


These polymers show good thermal stability and fire retarding properties. They are suitable for use as stabilizers in PVC and for surface coating. The following, organotin polyolefins are polymers which contain carbon-tin bonds in the backbone. They can be prepared by reacting tin halides or organotin halides with olefins, aluminium and hydrogen under pressure. Another method is polyaddition of organotin dihydride on diolefin.[11]

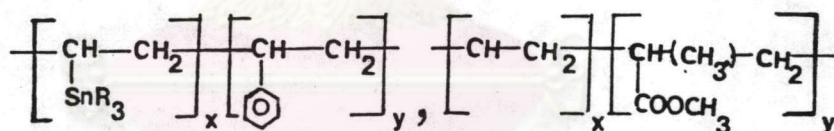$$n\ R_2SnH_2\ +\ n\ CH_2{=}CHR'CH{=}CH_2 \longrightarrow \left[ Sn(R)_2CH_2CH_2R'CH_2CH_2 \right]_n$$

### 1.5.2  Organotin Groups in Polymer Side Chains

### A.  Organotin Polyolefins

Organotin polyolefins are obtained by polymerization of monomers in which the vinyl group is not bonded directly with tin. It can be expected that when the olefinic groups is attached directly

to a tin atom(eg. $R_3SnCH = CH_2$) back donation of the pi electrons from vinyl group to the tin atom will deactivate the vinyl group. Hence polymerization is hindered. It was found that even using pressure as high as 6,000 atm at 120°c for 6 hr., only trimers were formed. Eventhough the trialkylvinyltin compounds could not be induced to homopolymerize, true copolymers, for examples, styrene-tributylvinyltin, methylmethacrylate, tributylvinyltin were obtained in the presence of styrene or methylmethacrylate and a radical initiator. It was reported that the rate of copolymerization decreased with increasing molar ratio of the vinyltin monomer. And the rate of homopolymerization of styrene or methyl methacrylate is greater than the organotin monomer unit. Thus, althougth reactions were carried out in equimolar ratio, the products were predominantly composed of polystyrene or polymethyl methacrylate block units.

$$\left[ \begin{array}{c} CH-CH_2 \\ | \\ SnR_3 \end{array} \right]_x \left[ \begin{array}{c} CH-CH_2 \\ | \\ \phi \end{array} \right]_y , \quad \left[ CH-CH_2 \right]_x \left[ \begin{array}{c} CH(CH_3)-CH_2 \\ | \\ COOCH_3 \end{array} \right]_y$$

where $y \ggg x$
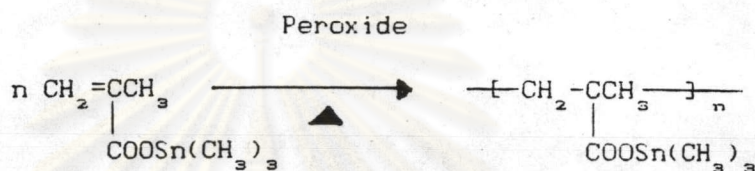
## B. Organotin Polymers with a tin atom in an ester group

As the carbon-tin bond is quite stable to hydrolysis, polyolefins containing alkyl-tin as functional groups are not very good biocidal polymers for antifouling paints. Polymers which containing carboxylic-tin bonds are very much prefered, because the organotin-ester linkage are able to hydrolyze in sea water. Thus the organotin biocide can be released and provide the antifouling action For this reason polymerization and copolymerization of (meth)acrylate organotin derivatives has been much more profoundly studied especially

in this thesis.

The polymerization reaction to form tri-alkyl-tin (meth) acrylate has been done by heating in the presence of free radical initiators such as peroxide or AIBN, in bulk, solution or emulsion (12). The general polymerization reaction to form organotin polyester is illustrated for the case of trimethyltin methacrylate.

$$n \ CH_2{=}CCH_3 \quad \xrightarrow{\text{Peroxide}} \quad {-}[CH_2{-}CCH_3{-}]_n$$
$$\underset{COOSn(CH_3)_3}{} \qquad\qquad \underset{COOSn(CH_3)_3}{}$$

A considerable number of organotin polyesters having the general structure

$$-[CR_2{-}CR'{-}]_n$$
$$\underset{COOSnR''}{}$$

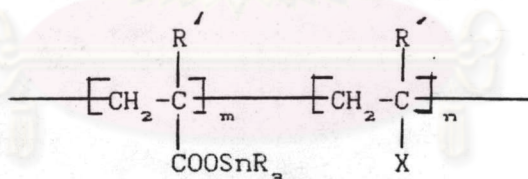where R and R' = H or alkyl

R'' = alkyl
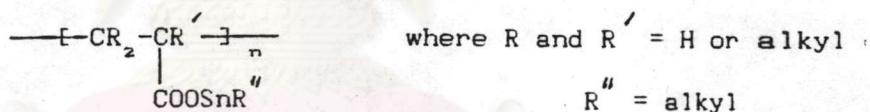
From a chemical point of view, the organotin ester function has little influence on the monomer reactivity. However, care must be taken to avoid experimental conditions which will destroy the carboxylate-tin bond, or any interaction between the initiator and the organotin group. The properties of the resultant polymers are influenced by the organotin moiety eventhough the polymerization conditions are not normally influenced by it. However, in a comparison study it was interesting to note that triphenyltin methacrylate polymerizes more rapidly than methyl methacrylate and tributyltin methacrylate polymerizes more quickly than butyl methacrylate under the same conditions. (13). But usually the polymerization rate of organotin acrylate or methacrylate is slightly lower than the equivalent organic

homologs. Free radical polymerization of methyl methacrylate in the presence of tetrabutyltin proceeds much slower, which is attributed to the mutual reaction of tin and benzoyl peroxide and the formation of complexes between the macroradical and tin compound (14).

Organotin polymers and copolymers usually give better mechanical properties than their carbon analog. (15) Except for the homopolymers of trialkyltin (meth)acrylate give poor physical properties of film-forming ( 16 ). So they are not sufficient to be used as sole binders in antifouling marine paints. In order to improve the physical properties, copolymers are often used. These tributyltin monomers have been copolymerized with appropriate ratios of unsaturated comonomers such as vinyl chloride, alkyl acrylate, alkyl methacrylate, styrene and acrylonitrile. The typical chemical structure of this organometallic copolymer is shown as follows

$$\left[ CH_2-\underset{\underset{COOSnR_3}{|}}{\overset{\overset{R'}{|}}{C}} \right]_m \left[ CH_2-\underset{\underset{X}{|}}{\overset{\overset{R'}{|}}{C}} \right]_n$$

$$R \ = \ alkyl \ group$$
$$R' \ = \ H \ or \ alkyl \ group$$
$$X \ = \ COOR, \ Cl, \ C_6H_5, \ CN$$

These copolymers have been synthesized to improve not only the physical properties of polymer film but also to increase the service life of the antifouling coating. It has been claimed that an improved antifouling coating was obtained from tributyltin-methacrylate-methyl methacrylate copolymer. This copolymer

released toxin by slow hydrolysis of the polymer. (17).

Polymers and copolymers from trialkyltin acrylate are widely used as antibacterial, antifungal and antifouling coating. (18) In other fields, these copolymers are used, for example as herbicides depending upon the slow released of toxic compounds . However, the polymerization of unsaturated organometallic compounds have not been extensively studied, inspite of many practical uses of these tin-containing polymers. It is an object ultimate of this work to study the polymerization of tributyltin acrylate and methacrylate with other (meth)acrylate comonomers.