

CHAPTER I



INTRODUCTION

1.1 Polymerization

Polymerization is a process to convert monomer molecules into a macromolecule. Two most important reactions are step-growth and addition polymerizations. Step-growth is characteristically formed by reactions involving the elimination of a small molecule, such as water, at each step. Addition polymerization results in the formation of a macromolecule which no such loss occurred.

The complete addition polymerization proceeds in three distinct stages : 1) initiation, when the active center which acts as a chain carrier is created; 2) propagation, involving the growth of the macromolecular chain by a kinetic chain mechanism and characterized by a long sequence of identical events namely the repeated addition of a monomer to the growing chain, 3) termination, where the chain growth is stopped by the neutralization or transfer of the active center (1-4).

When only one species of monomer is used to build a macromolecule, the product is called a homopolymer, normally referred as a polymer. It is often found that homopolymer have widely different properties and one might think that by using physical mixtures of various types, a combination of all the desirable properties would be obtained in the resulting materials.

Unfortunately, this is not always so, and instead it is more likely that the poorer qualities of each become exaggerated in the mixture(5).

An alternative approach is to try to synthesize polymer chains containing more than one monomer and examine the behavior of the product. By choosing two (or perhaps more) suitable monomers, a polymer chain incorporating these monomers can be prepared, and results in products of the better qualities than the parent homopolymers. This process is known as copolymerization (5).

Usually, copolymerizations are much more complex than those in a homopolymerization. For example, attempts to polymerize styrene and vinyl acetate result in copolymers containing only 1 to 2 percent of vinyl acetate while a small quantity of styrene will tend to inhibit the free radical polymerization. At the other extreme, two monomers like maleic anhydride and stilbene are extremely difficult to polymerize separately but form copolymers with relative ease (6).

It has been known that monomers differed markedly in their tendencies to enter into copolymers. The composition of copolymer being formed at any instant is given by the following equation which is known as the copolymer equation (7).

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \left[\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \right]$$

$[M_1]$ and $[M_2]$ are the concentrations of each of two monomers. The quantities r_1 and r_2 are the relative reactivity ratios defined more generally as the ratio of the reactivity of the propagating species with its own monomer to the reactivity of the propagating species with the other monomers. The ratio $[M_1]/[M_2]$ (feed ratio) varies during the copolymerization because one monomer may be consumed more rapidly than the other. However, it can usually be assumed that instantaneous feed ratios will not change significantly from the initially feed ratio if the copolymerization is only allowed to go to low conversion (1,5).

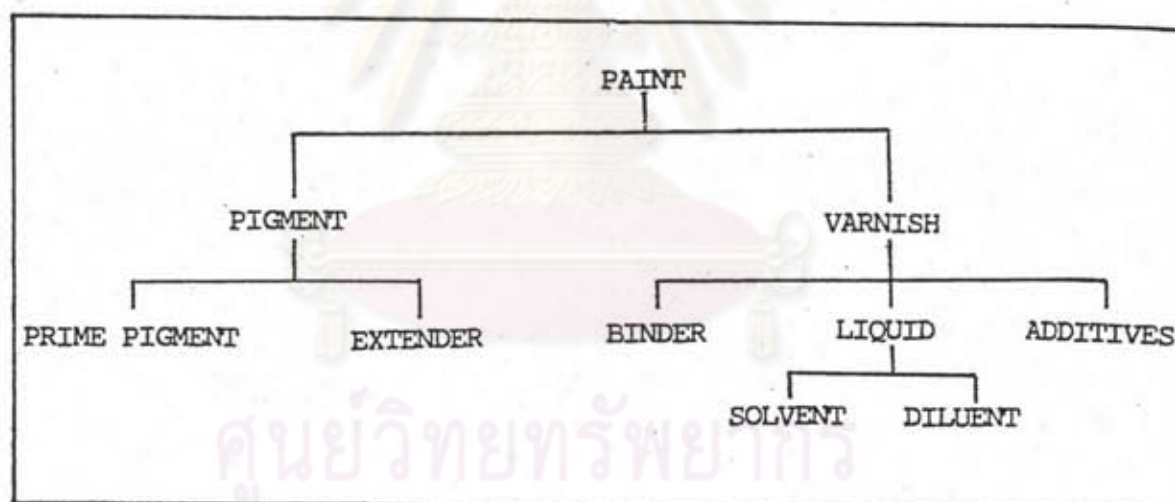
The copolymer equation provides a means of calculating the amount of each monomer incorporated in the chain from a given reaction mixture of feed, when the reactivity ratios are known. It shows that if monomer M_1 is more reactive than M_2 , then M_1 will enter the copolymer rapidly, consequently the feed become poorer in M_1 .

As r_1 and r_2 are obviously the factors which control the composition of the copolymer, one must obtain the reliable values of r for each pair of monomers (comonomers) if the copolymerization is to be completely understood and controlled. This can be achieved by analyzing the composition of the copolymer formed a number of comonomer mixtures with various $[M_1]/[M_2]$ ratios. The reactivity ratios are remarkable insensitive to environmental changer such as the presence of solvent, chain transfer agents, inhibitors or different types of free radical catalysts. Thus, the copolymer

composition will depend only on the relative monomer concentration in the feed (7, 8).

1.2 The composition in paints

This research work is focussed on the copolymerization between each of four fungicidal chlorophenyl acrylate monomers with vinyl acetate. Such reaction will lead to the incorporation of the chlorophenolic fungicides into poly(vinyl acetate) which is commonly used as the binder in paints(9). Therefore, some background in chemistry of paints should be briefly mentioned here.



Scheme 1 The composition in paint

Paint consists of pigment and varnish (Scheme 1). The pigment may be divided into two categories, namely prime pigment and

extender. Prime pigments provide color, hiding power and protection of the substrate by corrosion inhibition. Extenders are cheaper than prime pigments and are used as fillers. Thus pigments have both decorative and protective properties, but they rub off. Thus most paints contain the other part called varnish.

The varnish consists of the binder, thinning liquid and various additives. The binder is the film former and is usually a polymer of reactive components that form a polymer on curing. Therefore, the binder of film former binds together the pigment particles and hold them on the surfaces. It is difficult to attach coatings that are not fluid to any surface that is flat or gently curving. The fluidity of paint permits penetration into the most intricate crevices. This is achieved by dissolving the binder in the liquid portion which is usually a mixture of solvents.

Besides pigment and the binder, there are other additives present to insure stability in the container, proper application, characteristics, and satisfactory film properties. These are materials such as dispersants, inert or extender pigments, preservatives, antirust agents, fungicides, etc. Accordingly, a paint formulation may contain as many as 15 to 25 ingredients(10).

1.3 Polymer containing chemically bound fungicides

An ideal fungicides to be added in paint should be 1) highly toxic to fungi but of low toxicity to humans; 2) soluble or readily dispersible in the paint, so that it will not agglomerate in

the drying film; 3) nonvolatile, to avoid vaporization from the paint film; and 4) low in water solubility, to avoid leaching from the paint during rainy weather. None of the commercially available fungicides meet all of these requirements. Furthermore, the other disadvantage is their finite lifetime in the film since they are simply added to the paint. Daily exposure to sun, rain, wind, heat, etc. will cause eventual loss of protection by leaching, evaporation and migration (11-23).

Recently, much attention has been paid on the development and use of polymers containing chemically bound fungicides. There are several advantages of chemically anchoring the fungicide to the binders, as compared with simply blending it into paint.

Since the polymer-attached fungicide would be dispersed molecularly along the polymer chain, it would not agglomerate into discrete particles as the film dried. Instead, it would remain dispersed in the form of a "solid solution", available wherever it eliminated because the fungicide would be part of the polymer. Furthermore, the fungicide would represent only a small weight percent of the polymer and for this reason, would not greatly affect the physical properties of the polymeric binder. Since the fungicide would be part of a macromolecule, humans would not be exposed to toxic vapor(15).

Fungicidal compound may be bonded to the polymer through a functional group which later can be hydrolyzed to free the fungicide. Some attractive functional groups include amide, ester,



and glucoside linkages. The hydrolytic process could, potentially, occur in two ways. First, environmental conditions might foster slow hydrolysis and liberate the fungicide. The rate of such a reaction, however, might be negligible, and it might be found that fungicide release would accelerate only under conditions of microbiological attack on the paint film. In this concept,

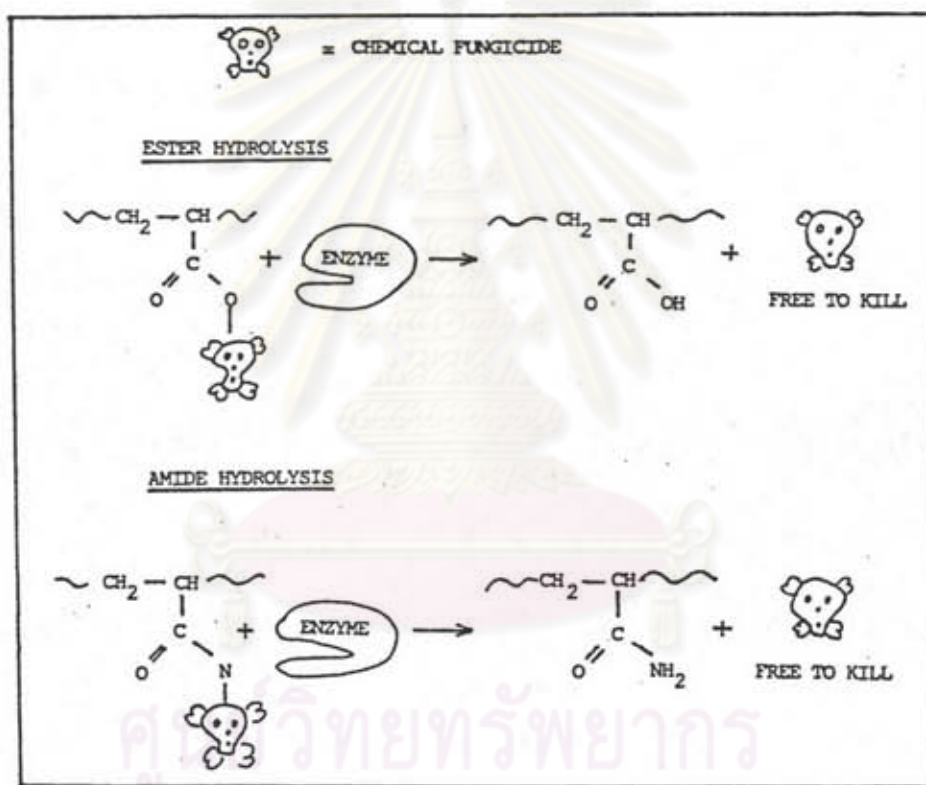


Figure 1.1 A polymer releasing fungicide on attack by fungi

extracellular enzymes (such as amidases and esterases) from the microorganisms would, themselves, cleave the fungicides (Figure 1.1) (15).

A detailed literature search revealed that little work had been done with the concept of polymer-anchoring a fungicide. Drisco and coworkers prepared paint resins containing tri-n-butyltin acrylate (Figure 1.2). Laboratory tests indicated these resins were resistant to some microorganisms and that fungicide leaching from the coating was considerably reduced compared to the use of the blended fungicide. However, field tests of these coating resins on pine and redwood test panels began to show microorganism growth after three months (25, 26).

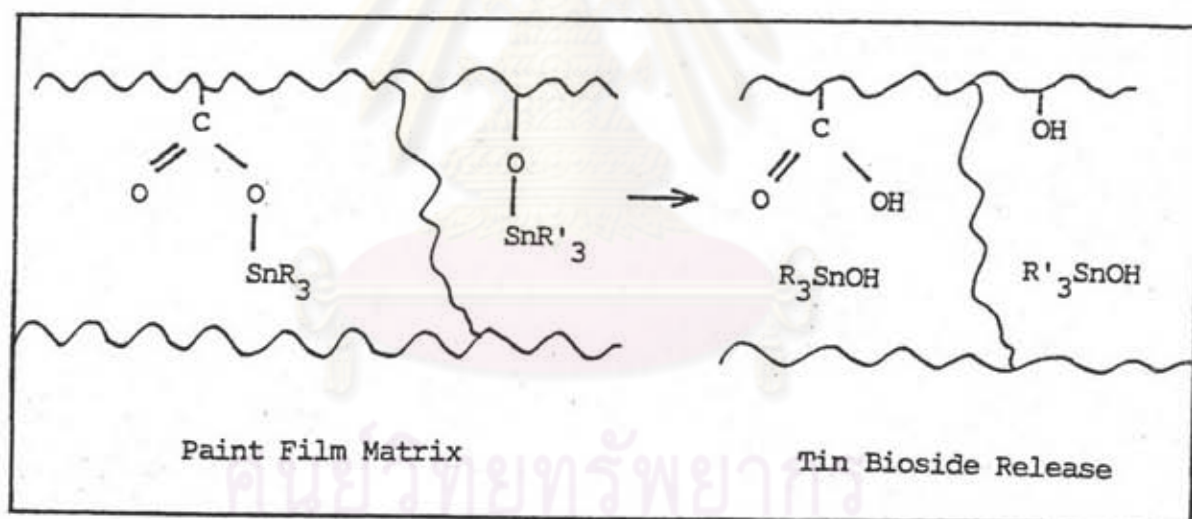


Figure 1.2 Control release organotin

Pittman and his coworkers are the only group who worked on the copolymerization of ethyl acrylate, vinyl acetate, n-hexyl methacrylate, n-butyl acrylate, methyl methacrylate and n-butyl methacrylate with nonmetallic fungicidal acrylates. The

fungicides which were used for their study were as following; pentachlorophenol, 8-hydroxyquinoline, 3-4-5-tribromosalicylanilide, o-benzyl-p-chlorophenol, salicylanilide, 2-(4'-thiazoyl) benzimidazole and 2-mercapto-pyridine-N-oxide (27-30).

1.4 Objectives

In this study, four nonmetallic fungicidal monomers were prepared for subsequent homopolymerization and copolymerization with vinyl acetate. These compounds will be tested for possible activity against microorganism growth. Pentachlorophenyl acrylate is solid with high melting point as compared to the other fungicidal monomers reported, it was chosen as a model compound. The other three fungicidal monomers are 2,4,6-trichlorophenyl acrylate, 2,4,5-trichlorophenyl acrylate and 4-chloro-3-methylphenyl acrylate which are the novel compounds as revealed by literature. However, whether they retard organism growth or not, the investigation of copolymerization kinetics for the chlorophenyl acrylate - vinyl acetate is desired. The reactivity ratios obtained for each system will be reported. To our knowledge these values were not mentioned in the literature, except for pentachlorophenyl acrylate-vinyl acetate system (28).