CHAPTER I

INTRODUCTION

1.1 Copolymerization

Polymerization is a process to convert monomer molecules into a macromolecule. Therefore, copolymerization is most useful defined as polymerization in which two or more structurally distinct monomers are incorporated into the same polymer chain (1-3). This involves a definite chemical reaction between monomer M_1 and M_2. Two most important reactions are condensation and addition polymerization. Condensation 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.

Free-radical copolymerization reactions are very closely related to addition polymerization reactions of single olefin monomers in that both proceed by a typical chain reaction with discrete initiation, propagation, and termination steps. Nevertheless, the simultaneous polymerization reaction of two olefin monomers often show rate and mechanism characteristics considerably different from those of homopolymerization reactions of either monomer alone. That is, the two monomers enter into the copolymer in overall amounts determined by their relative con-centrations and reactivities.

The behavior of monomers in copolymerization is especially useful for studying the effect of chemical structure on reactivity.

Furthermore, copolymerization allows the synthesis of an almost unlimited number of different products by variations in the nature and relative amounts of the two monomer units in the copolymer product, while homopolymerization is relatively limited (2).

However, compatibility with respect to chemical reactivity of a monomer with other monomer is essential for copolymer formation which lead to new products with unique and valuable properties. For example, polystyrene is a brittle plastic and has limited practical utility, while copolymerization of styrene with butadiene leads to electromeric properties which greatly increases the usefulness of polystyrene.

1.2 Monomer Reactivity Ratios

When two monomers are copolymerized it is common to characterize the reaction in terms of monomer reactivity ratios which define the rate constant for a given chain and adding its own monomer relative to that of the same chain and adding the other monomers. These reactivity ratios represent a rich source of information which not only can be used to describe copolymerization, but can also be used to study the relation between structure and reactivity in radical addition reaction.

Monomer reactivity ratios has been determined for a large number of copolymer systems (4). It was found 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 copoymer equation (1-3).

$$\frac{d[M_1]}{d[M_2]} = \frac{([M_1]/[M_2]).r_1+1}{([M_2]/[M_1]).r_2+1} \qquad (1)$$

$[M_1]$ and $[M_2]$ are the concentrations of each of two monomers in the monomer feeding, while $d[M_1]$ and $d[M_2]$ are their corresponding concentrations in the copolymer. The monomer reactivity ratios r_1 and r_2 are defined as the ratios of the reactivity of the propagating species with its own monomer to the reactivity of the propagation species with the other monomers.

Monomer reactivity ratio can be considered by several methods (5-11) based either on the differential [eq.(1)] or on the integral copolymer equations. The differential copolymer equation [eq.(1)] describes the composition of the instantaneously formed copolymer as a function of the relevant monomer feed composition only. Therefore, it is obvious that in copolymerization experiments in which calculation procedures of monomer reactivity ratios are based on eq. (1), the conversion to copolymer has to be kept as small as possible (12).

The Fineman-Ross method is one of several methods to compute monomer reactivity ratios, based on the differential equation and on data consisting of the initial monomer and the resulting copolymer composition. There are three factors that introduçe systematic errors in the calculated reactivity ratios (5,6):

(1) The ratio of the instantaneous monomer consumption is approximated by the copolymer composition.

(2) Most copolymerization reactions inevitably show a drift of the molar feed ratio and so the differential is only approximately valid.

(3) the reactivity ratios are computed, using simple least-square methods, thereby neglecting the error in the so-called independent variable. Because of factors (1) and (2) the differential copolymer equation is only approximately valid.

Integration of eq.(1) yields an exact relationship between the changing monomerfeed ratio and the degree of conversion. Most copolymerization reactions, regardless of the experimental technique applied, will inevitably show a drift in the molar feed ratio as the degree of coversion increases. For this reaction the integrated form should be preferred over the differential form of the copolymer equation in reliable calculation procedures for reactivity ratios. Because the error due to factor 1 and 2 does not exist in this case.

The determination of monomer reactivity ratios using the integrated form due to Mayo and Lewis (11) involves compositional analysis of monomer feed and conversion. However, the reactivity ratios which are estimated from this method are inaccurate if a drift of the intersection points as a function of the monomer feed composition is observed (13). The disadvantage of this method is treatment of the data which complex calculations are required.

1.3 A Controlled Release Fungicide Concept

Coatings are applied to exterior substrates not only for their decoration effect but also for the protection of the substrate from deterioration due to the environment. Mildew or fungal growth on the surface produces unsightly black discoloration and can penetrate the underlying substrate causing detectable damage. In fact, estimates of losses due to mildew defacement exceed one million dollars annually (14). Thus, mildew defacement is recognized as a serious problem, especially in areas of high humidity.

Conventional solutions to the mildew defacement problem involve the incorporation of one or more of a large number of commercially available antifungal agents into the paint. This approach has met with varied degress of success with respect to the duration of mildew protection. Basically, there are four major problems associated with the failure of most non-mercurial fungicides after a relatively short period of time. They are:

(1) Leaching from the film due to the porous nature of films produced by latex paints and the solubility of the fungicide.

(2) Evaporation or volatilization due to the physical properties of the fungicide and the climatic conditions.

(3) Photo-degradation due to the chemical properties of the fungicide during exposure to sunlight.

(4) Reaction with other paint components due to the functional groups present in the molecular structure of the fungicide.

The use of mercurial fungicide has been severely curtailed or is non-existent due to the fear of environmental damage. Thus, the major problems associated with current systems are a short period of utility and/or environmental damage.

The proprosed solution to these problems involves the application of controlled release concept. Many design concepts have been studies in developement of controlled-release formulations for fungicides. One of the basic controlled release concepts using chemical bonding of a fungicide to a natural or synthetic polymeric material, as by pendant ester or anhydride linkages, which control the release of the agent by hydrolysis, etc. is indicated conceptually in Figure 1.1 (15,16). The theoretical comparison of the rate of loss of fungicide from a film for a typical free fungicide and a controlled release (constant rate) fungicide is shown in Figure 1.2 (14,17). Clearly, an increase in the duration of mildew inhibition can be expected with the controlled release fungicide. In addition, an economical advantage can be excepted (Figure 1.3) through a reduction in the amount of fungicide required for the same level of control. Obviously, the fungicides already in use can be improved to minimize the waste of the costly and toxicchemicals and to extend the duration of fungicidal effective-ness.

The advantages derived from the use of controlled release concept include longer term protection, use of less toxicant, and reduced emission of toxicant into the environment. Indeed, controlled release through the use of chemically anchored fungicides has already recieved the attention of Pittman et. al. (18-22) and other polymer-bound toxicants have been successfully utilized as herbicides (23). Therfore, this approach deserves serious consideration as a solution to the mildew defacement problem.

1.4 Background on Polymer-Bound Fungicide

Several problems are encountered when an organic fungicide is simply mixed into a paint (24). The most serious one is that the fungicide tends to be leached or vaporized from the paint film over long time periods. Daily exposure to sun, rain, wind, heat, etc. will cause eventual loss of protection by leaching, evaporation and

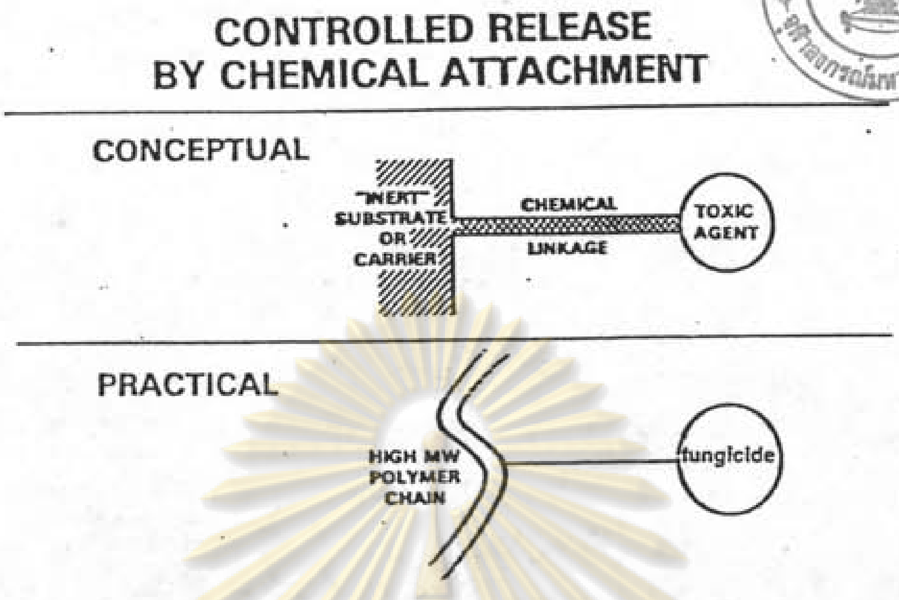


Fig. 1.1

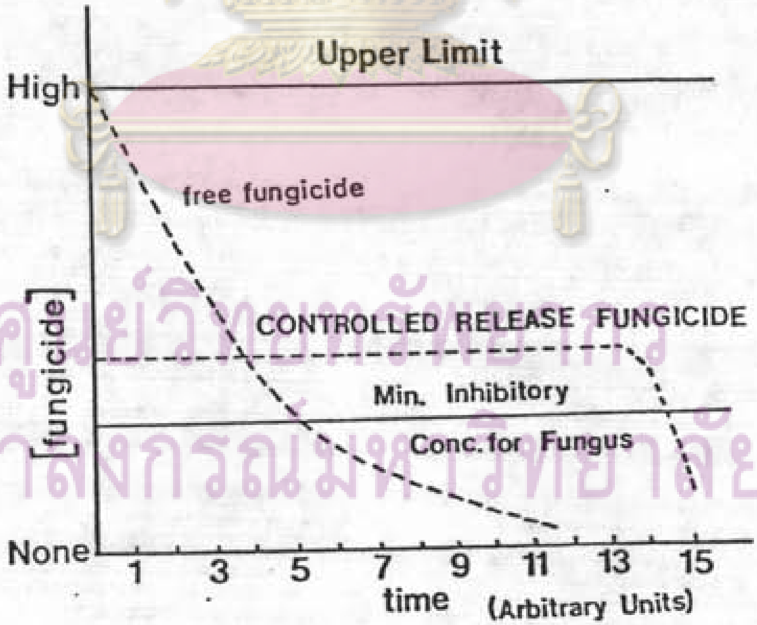


Fig. 1.2 Rate of loss of free fungicide and controlled release fungicide

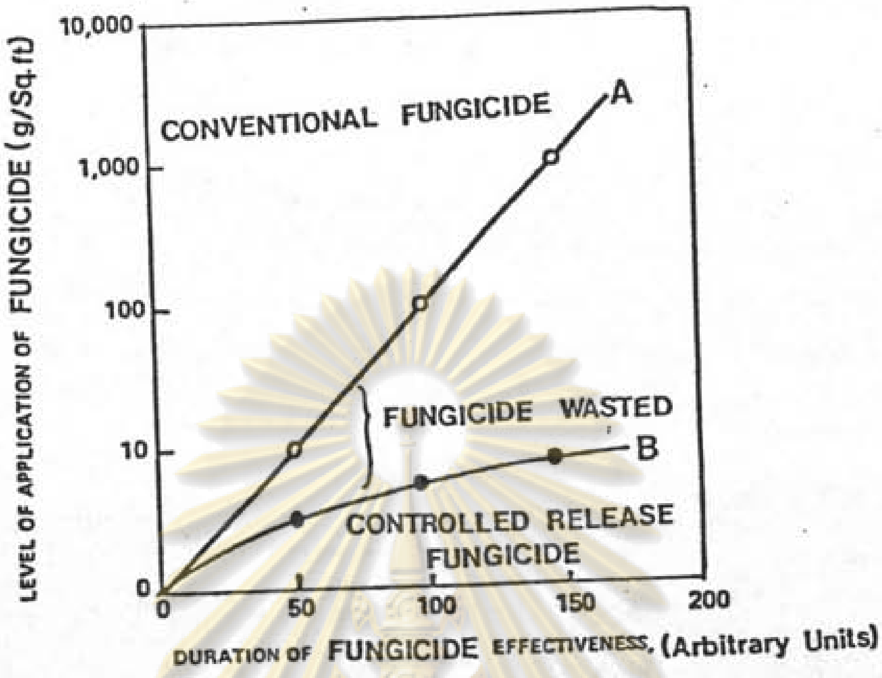
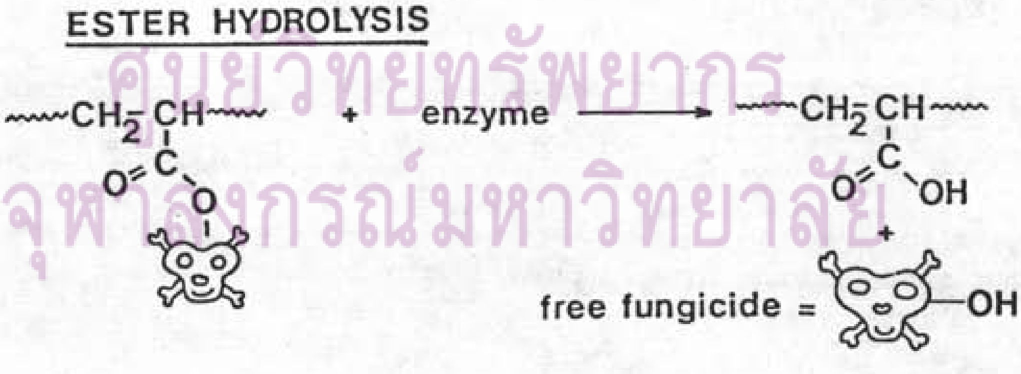


Fig. 1.3 Comparison of level and duration of effectiveness of conventional and controlled release fungicide



Scheme 1.1 A polymer releasing fungicide on attack by fungi

migration (19, 22, 25-35). After the concentration of fungicide drops below critical levels, mildew may start growing on the coating surface (25). However, the losting fungicide could further be harmful to the environment and to humans.

Recently, much attention has been paid on the synthesis of the polymers containing chemically anchored fungicides. There are several advantages of chemically anchoring the fungicide to the binder, as compared with simply mixing it into the paint. since the polymer attached fungicide would be molecularly dispersed along the polymer chain, it would not agglomerate into discrete particles as the film dried. Solubility, volatility and migration problems would also be eliminated. Furthermore, the fungicide would respresent only small mole percents of the polymer and for this reason, would avoid changing substantially the physical properties of the polymeric binder (i.e., Tg, etc.).

A fungicidal compound may be attached 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. Though the hydrolytic process could, potentially, occur under the environmental conditions, it might be found that fungicide release would accelerate only under conditions of microbialogical attack on the paint film. In the latter concept, exocellular enzymes from the microorganisms would, themselves, cleave the fungicide (scheme 1.1). This mode of hydrolysis would supply the fungicide only when needed.

A detailed literature search revealed that little work had been done with the concept of polymer-anchoring a fungicide. The copolymerization of vinyl acetate, acrylic monomers with fungicidal acrylates was prepared by Pittman et. al. (18, 20, 21). The fungicides chosen for their study were as followings; pentachlorophenol, 8-hydroxyquinoline, 3,4,5-tribromosalicylanilide, o-benzyl-p-chlorophenol, salicylanilide,2-(4'-thiazoyl)-benzimidazole and 2-mercapto-pyridine-N-oxide.

More recently, Mrs. Tantayanon (37) synthesized poly(methyl methacrylate) containing chemically bound the fungicidal chlorophenyl acrylate. Three fungicides, i.e., pentachlorophenol, 2,4,5-trichlorophenol and 4-chloro-3-methylphenol were chosen for her study. Only small amount of fungicidal monomer (1-5 % by mole) has been copolymerized with methyl methacrylate to keep the properties of the synthesized copolymer close to poly (methyl methacrylate). Although, the copolymers could be fungicidal to a variety of some microorganisms, they seem a little less active than the free parent fungicide.

However, no detailed study of the copolymerization kinetics for such monomers has been mentioned. In order to know the monomer reactivity ratios of each system, this study deals with the copolymerization of methyl methacrylate with the fungicidal monomers. Firstly, four fungicidal monomers, i.e., pentachlorophenyl acrylate (PCPA), 2,4,5-trichlorophenyl acrylate (2,4,5-TCPA), 2,4,6-trichlorophenyl acrylate (2,4,6-TCPA) and 4-chloro--3-methylphenyl acrylate (4-Cl-3-MPA), were prepared for subsequent homopolymerization and copolymerization with methyl methacrylate.