CHAPTER I

INTRODUCTION
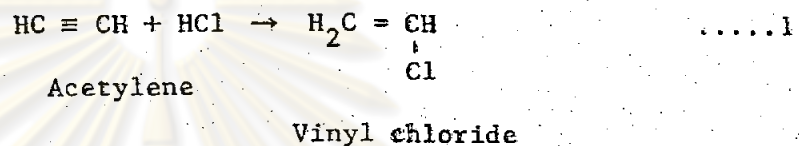
1.1 Poly (vinyl chloride)

Poly (vinyl chloride), commonly known as PVC, is a synthetic thermoplastic polymer. It is a white powder and decomposes at $148^{o}C$, evolving toxic fumes of hydrogen chloride (1).
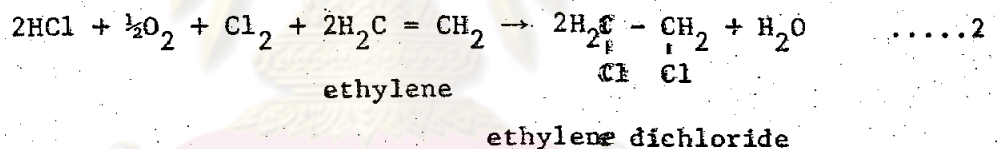
PVC has a sales volume between polyethylene and polystyrene. The Stanford Research Institute predicts that by the year 2000 in the United States, PVC will be the leader, with an annual volume of 17×10^{9} metric tons (2). This widespread use arises from a high degree of chemical resistance and a truly unique ability to be mixed with additives to give a large number of reproducible PVC compounds with a wider range of physical, chemical and biological properties than any other plastic material (2-5). PVC products have been known and welcomed by consumers for several applications (6-8) such as piping and conduits of all kinds; siding; gutter; window and door frames; officially approved for use in interior piping, plumbing and other construction uses; raincoats, toys, gaskets, garden hose, electrical insulation, shoes, magnetic tape, film and sheeting; container for toiletries, cosmetic, household chemicals; fibers for athletic supports; sealant liners for ponds and reservoirs; adhesive and bonding agent, plastisols and organosols; tennis court playing surfaces; flooring; coating for paper and textile; wire and cable protection; base for synthetic turf; phonograph records.

1.2 Preparation of poly (vinyl chloride)

Poly (vinyl chloride) was prepared by polymerization of vinyl chloride using peroxide as the initiator. Commercial production of vinyl chloride monomers starts with either of two raw materials: acetylene or ethylene (9). With acetylene feed, the synthesis is completed by the simple addition of hydrochloric acid (Eq. 1).

$$HC \equiv CH + HCl \rightarrow \underset{\underset{Cl}{|}}{H_2C} = CH \qquad \dots\dots 1$$

Acetylene

Vinyl chloride

An oxychlorination reaction (Eq. 2) is used with an ethylene base feed to produce ethylene dichloride.

$$2HCl + \tfrac{1}{2}O_2 + Cl_2 + 2H_2C = CH_2 \rightarrow 2H_2\underset{\underset{Cl}{|}}{C} - \underset{\underset{Cl}{|}}{CH_2} + H_2O \qquad \dots\dots 2$$

ethylene

ethylene dichloride

Then the ethylene dichloride is dehydrochlorinated to form vinyl chloride (Eq. 3).

$$\underset{\underset{Cl}{|}}{H_2C} - \underset{\underset{Cl}{|}}{CH_2} \rightarrow \underset{\underset{Cl}{|}}{H_2C} = CH + HCl \qquad \dots\dots 3$$
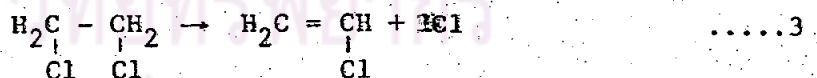
Although vinyl chloride monomer can be produced by either of the above reaction , current economics favor the ethylene approach because ethylene is considerably lower in cost than acetylene. Thus, most new vinyl chloride plants are utilizing the oxychlorination route.
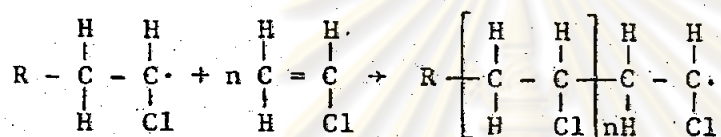
Polymerization of vinyl chloride monomer is a radical chain reaction(3,10) which may be triggered off by energy from a natural source (light) or an artificial source (electron beam) or by a radical-

forming catalyst. When the initial radical has been formed, a series
of monomers attach themselves to such radical and the double bond in
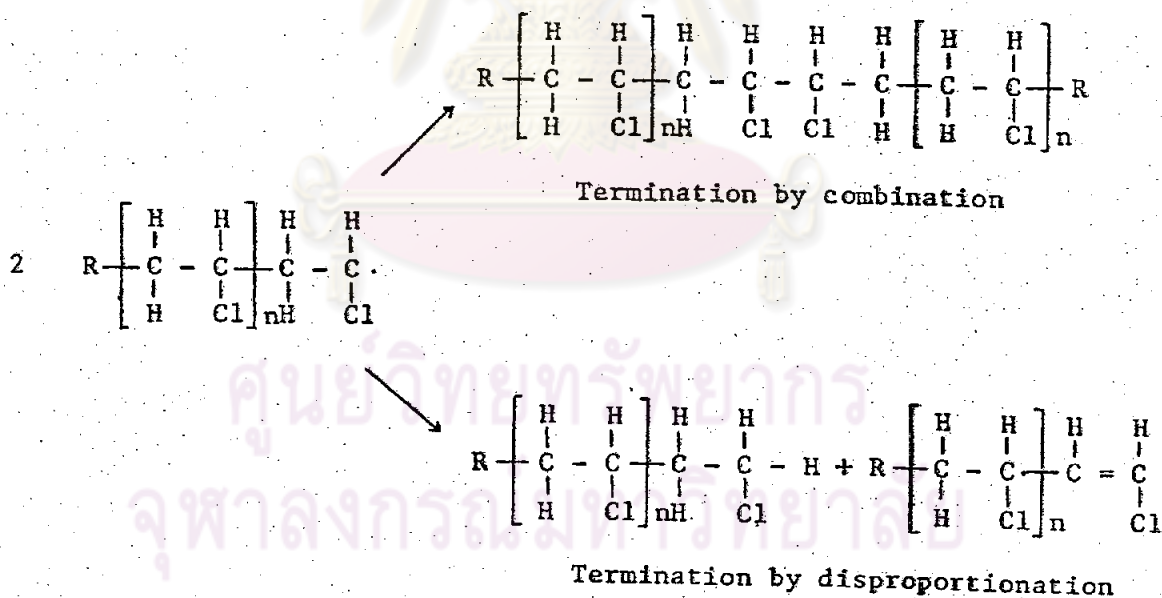the vinyl chloride is broken (SCHEME 1-1).

Initial reaction:

$$R\cdot + \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} = \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} \rightarrow R - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}\cdot \qquad R\cdot = \text{initial radical}$$

Propagation reaction:

$$R - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}\cdot + n\,\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} = \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} \rightarrow R \left[\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} \right]_{nH} \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}\cdot$$

Termination reaction:

$$R \left[\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} \right]_{nH} \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} \left[\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} \right]_{n} R$$

Termination by combination

$$2\; R \left[\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} \right]_{nH} \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}\cdot$$

$$R \left[\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} \right]_{nH} \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} - H + R \left[\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} \right]_{n} \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} = \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}$$

Termination by disproportionation

SCHEME 1-1 Polymerization of vinyl chloride(10)

The radical function is maintained as the chain grows until finally a
termination reaction occurs. This can be the result of a combination
of two macroradicals or of a disproportionation reaction.

There are four basic manufacturing processes for PVC production namely suspension, mass, emulsion and solution. In each process, polymerization is initiated by free radical produced by thermal decomposition of peroxide-type initiators and proceeds exothermally at temperature of 40 to $70^{\circ}C$ (3). Vinyl chloride is a gas at room temperature (b.p.$-13.9^{\circ}C$)(11). Thus the reaction is carried out in pressure vessels equipped agitators and heat-removal systems capable of precise temperature control.

In the suspension process, which is the most preferred one(6), vinyl chloride droplets are suspended in water by means of protective colloids such as polyvinyl alcohol, gelatin or methyl cellulose and rapidly agitated. Reactions, which may take up to 10 hours, are carried to a predetermined end point since they do not go to completion. Unreacted monomer is removed from the vessel by vacuum and is stripped from the slurry. The slurry is largely dewatered in a centrifuge and then dried. The number average molecular weight of PVC thus prepared are usually on the order of 60,000 (9).

1.3 Deterioration of poly (vinyl chloride)

Although poly (vinyl chloride) is used extensively for outdoors application but one disadvantage of PVC is its unstability to heat and light (12,13). However, thermal degradation of PVC is particularly observed at temperature above $200^{\circ}C$ (14,15). When it is exposed to sunlight, only light thus induces damage to PVC. The portion of the electromagnetic spectrum most directly responsible for light induced deterioration in polymer is the ultraviolet region falling between 290 and 400 nanometers (16,17). High-energy radiation (cosmic rays, gamma rays) and ultraviolet radiation of wavelength shorter than 290 nanometers are also capable of rupturing chemical bonds, but these wavelengths are

not found at the earth's surface, owing to the filtering action of the atmosphere formaldehyde, carbon dioxide and ozone. Visible light (400-700 nanometers) is considerably weaker and is not sufficient to rupture most chemical bonds. FIGURE 1-1 shows the spectral energy distribution of daylight.
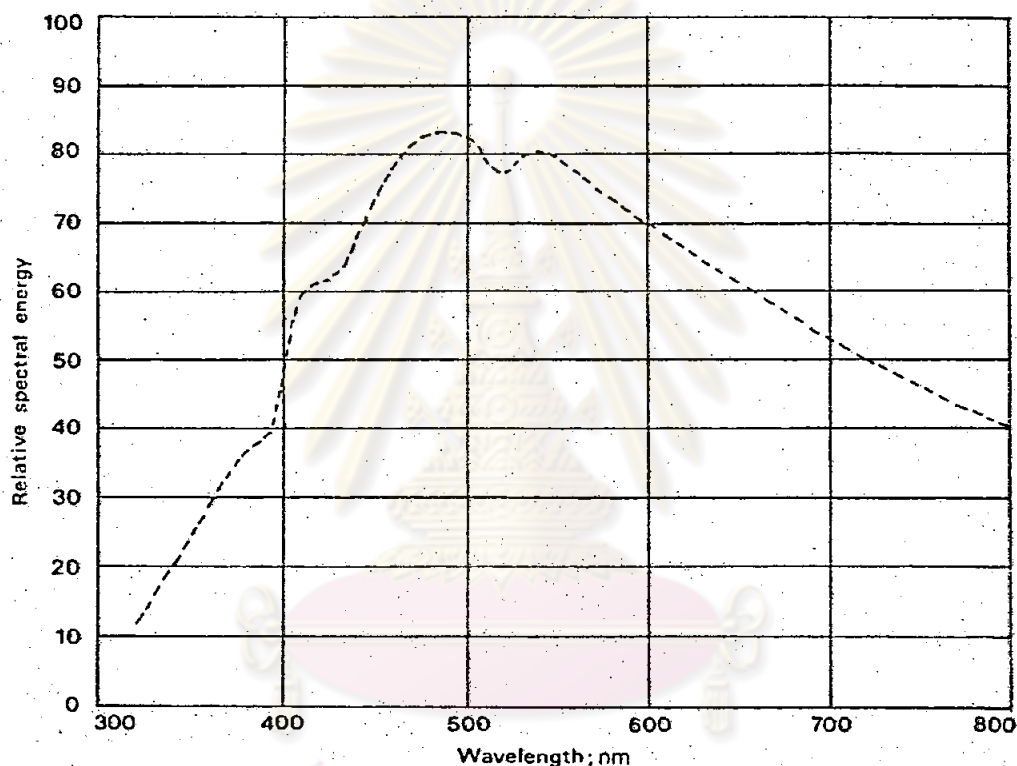
FIGURE 1-1 Spectral energy distribution of daylight (10)

After ultraviolet irradiation of PVC, it splits off hydrogen chloride. The elimination of the first molecule of hydrogen chloride and the subsequent formation of an unsaturation (double bond) on the PVC chain then activates the neighbouring chlorine atom(18), which is now structurally located as an allylic chloride and thus facililates the subsequent elimination of another hydrogen chloride molecule, with the process continuing to repeat itself (SCHEME 1-2).
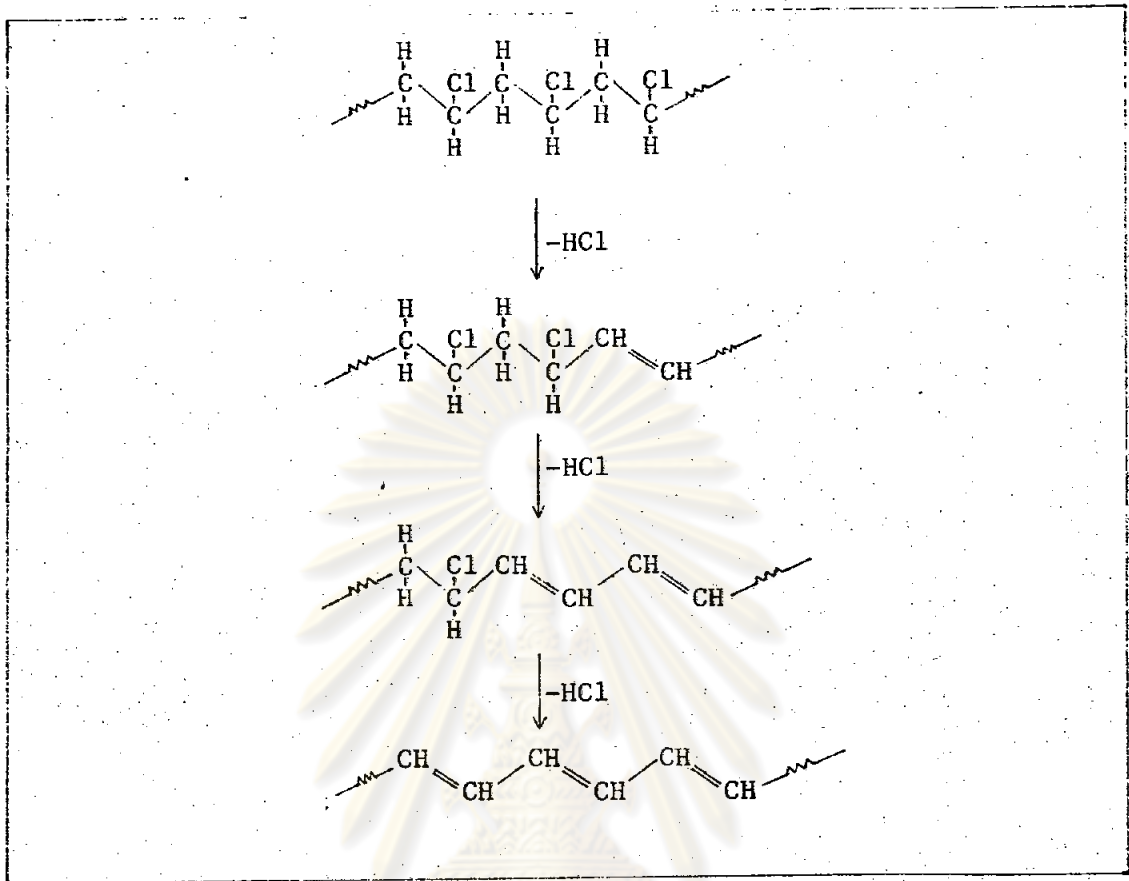
SCHEME 1-2   Evolution of hydrogen chloride in PVC

This progressive dehydrochlorination proceeds quite rapidly, soon

leading to a chain segment of polyunsaturation and the polymer is

discoloured.(18-19)   The formation of visible colour usually is the

first evident indication of degradation, although chemical methods also

indicate the evolution of hydrogen chloride.   These changes occur before

any of hydrogen more serious manifestations of degradation become

evident.   Initially, the polymer undergoes some chain scissioning,

leading to a gradual degradation of mechanical properties and chemical

resistance.   This is soon accompanied by cross-linking, with in the

later stage predominated.   Rapid oxidation of the polyene sequences

also occurs, leading to the formation of carbonyl and hydroperoxide

groups.(18)

Since poly (vinyl chloride) contains only C-C, C-H and C-Cl bonds, it is expected that PVC should not absorb ultraviolet light of wavelength longer than 190 nanometers. Measurements of ultraviolet absorption spectra of PVC show an increased rapid absorption below 220 nanometers and a low absorption at 320 nanometers (20). Furthermore the free radicals were observed during ultraviolet irradiation of PVC. These evidences indicate the presence of some kinds of chromophores. Also, small quantities of external impurities which were not removed in the purification process may be responsible for the absorption of light above 190 nanometers. The most probable chromophores present in PVC are carbonyl groups which formed during the polymerization process in the presence of air (20) and olefin end groups which formed by the chain termination due to disproportionation(10) (SCHEME 1-1). When these chromophores absorb light, they could be responsible for the photoinitiation process.

1.4 <u>Photodegradation of solid Poly (vinyl chloride)</u>

There is enormous amount of literature on the cause and effects of degradation in PVC, and there is general agreement of fundamental in spite of many differences on points of detail. The main features indicated by available evidences may be briefly summarised as follows.

Alkene sensitization of the photodegradation of PVC seems to be supported by other observations that have been reported in the recent literatures. One of these is the increase in rates of nonoxidative photodegradation that have been found for polyene which were subjected to a preliminary nonoxidative thermal treatment (21). Also of interest in this regard is the production of free radical during the ultraviolet irradiation of PVC under vacuum apparently can be sensitized by polyenes

that have been created during a preliminary photolysis (22).

However other workers have detected a significant amount of photodehydrochlorination during irradiation at $30^{\circ}C$ under air with a high-pressure mercury lamp(23) and they found that the rate of this process increase with temperature. When molecular oxygen is absent, the average length of the conjugated polyene formed during ultraviolet irradiation of PVC have been found to increase with increasing temperature (24).

On the other hand, radicals are undoubtedly involved in the photodegradation of PVC under some experimental conditions. Recent ESR study has provided the evidence for the formation of alkyl and allyl-type radicals during the low-temperature ultraviolet irradiation of the polymer (25). Peroxy radicals were also observed when molecular oxygen was present. Other ESR work has shown convincingly that the radical $-CHCl-CH_2-\overset{\bullet}{C}H-CH_2-CHCl-$ results from the irradiation of PVC at liquid-nitrogen temperature (26).

It was noticed that, much attention has recently been paid on the photodegradation of PVC. However, only solid PVC has been studied. On the surface of PVC the reaction would occur. Therefore in this work it is worthwhile to study the photodegradation of PVC in the form of solution in order to make PVC molecule homogeneously react with the radiation. Various factors influencing the photodegradation of PVC in solution will also be studied.

In this work, the conductometric measurement of hydrogen chloride produced from the photodegradation of PVC will be used.