

CHAPTER II

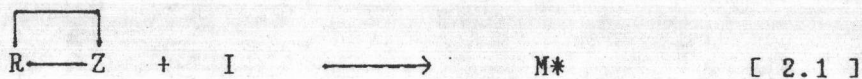
THEORY

As this study deals mainly with the synthesis of two biodegradable polymers, poly(ϵ -caprolactone) and methylacrylate grafted starch, thus two types of polymerization are reviewed here as basic considerations. The linear poly (ϵ -caprolactone) can be obtained from the ring-opening polymerization of cyclic monomer, ϵ -caprolactone while polymethylacrylate can be grafted onto starch by the suspended graft copolymerization.

2.1 Ring-opening polymerization

2.1.1 General characteristics (26)

The ring-opening polymerization of cyclic monomers has been initiated by various initiators which are both ionic and molecular species. Initiators results in opening of the ring to form an initiator species, M^* , which may be either an ionic or neutral molecule depending on the initiator.



Where Z represents the functional group on the monomer molecule and I is symbolized for the initiator. The examples of

the initiators used for ionic ring-opening polymerization are Na, RO, HO, and BF₃. The prime initiator of the molecular type is water. The more reactive and stronger ionic initiators are essentially required by most monomers. On the other hand, the molecular type initiators are required by only the more reactive cyclic monomers to undergo polymerization.

The initiator species, M*, grows by the successive ring-opening additions of many monomer molecules.



The nature of the chain-growth in the ring-opening polymerization bears a superficial resemblance to that in the chain polymerization. However, the ring-opening polymerizations are able to have the characteristics of either chain or step polymerization or of both. The classification of the ring-opening polymerizations as chain or step polymerizations is based on the two considerations, experimentally observed kinetic laws and the distribution of polymer molecular weights with time. Each of the ring-opening polymerizations is either a step or a chain polymerization depending on its characteristics.

The ease of polymerization of cyclic monomers depends on thermodynamic and kinetic factors. The relative stabilities of the rings and according linear structures including enthalpy, entropy and free energy changes for conversion of cyclic monomers

to the linear polymer are considered as thermodynamic factors which determine whether a cyclic monomer can be converted to linear polymer. Not only the thermodynamic feasibility does guarantee the actual polymerization of cyclic monomers, but the kinetic path way also be required for the ring to be opened and undergo polymerization.

2.1.2 Ring-opening polymerization of cyclic monomers

There exist many cyclic monomers that can undergo ring-opening polymerization in the presence of initiators under the suitable conditions. These monomers are cyclic ethers, cyclic amides, cyclosiloxanes, and cyclic esters or lactones (27). Each of cyclic monomers requires different types of the initiators on which the types of polymerizations and their mechanisms depend. Most cyclic ethers preferably undergo cationic ring-opening polymerization, except to the epoxides which can be polymerized by both anionic and cationic initiator due to the high degree of strain in the small 3-membered ring.

Cyclic amides can be polymerized by initiation of all types of the initiators, cationic, anionic, and water. The last one is referred to the oldest and yet most important initiator for ring-polymerization since it has been used in commercial process for producing polyamides. Anionic initiation is also practical for commercial manufacturing. However, cationic initiation is not useful because the conversions and polymer molecular weights

that can be obtained are not high enough. The productions of Nylon-6, Nylon-12, and to a lesser extent, Nylon-8, are, for instance, of commercial importance.

Cyclosiloxanes are the compounds containing Si-O ring in which Si and O atoms are alternately bonded together. The ring containing 3-Si and 3-O atoms, is called cyclotrisiloxane (D_3), can be polymerized by anionic initiators in the presence of donor solvents such as THF (28, 29), diglyme (30), DME (31), and HMPA (31). The cyclotrisiloxanes can undergo rapid polymerization to give near monodisperse polymers. Cyclo-tetrasiloxanes (D_4) containing 4-Si and 4-O atoms, can also be polymerized but its rate of polymerization is much lower than that of D_3 .

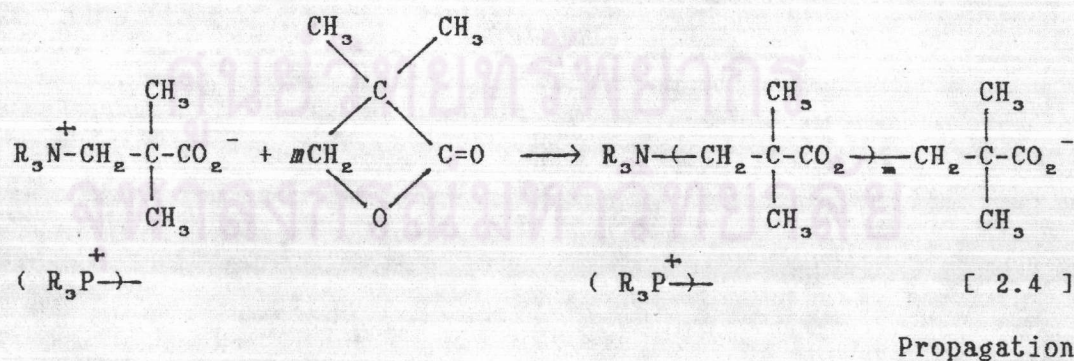
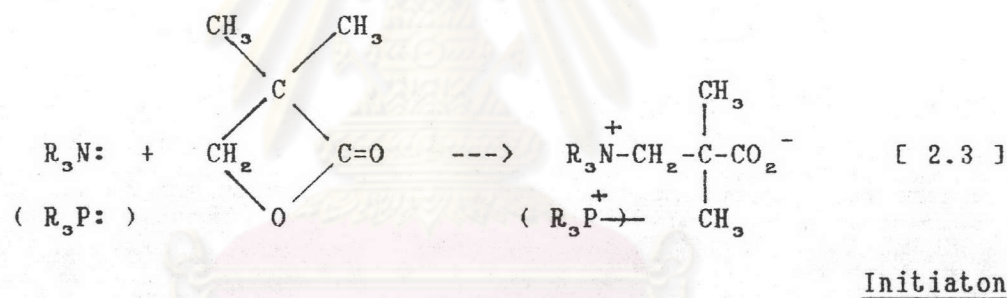
Among variety of ring opening polymerizations, that of lactone or cyclic ester monomers seem to be more interesting since they give polymers with ester backbone or polyester. Aliphatic polyesters are found to be active to enzymic hydrolysis and considered as a potential biodegradable polymers (32,33).

2.1.3 Ring-opening polymerization of lactone

The polymerizations of lactones have been studied widely. The ring-opening reactions of lactones can give homopolymers, copolymers and terpolymers depending on numbers of the type of monomers used. The lactones are classified into

groups and according nomenclature are given. The polymerizations of lactones are briefly discussed as follows:

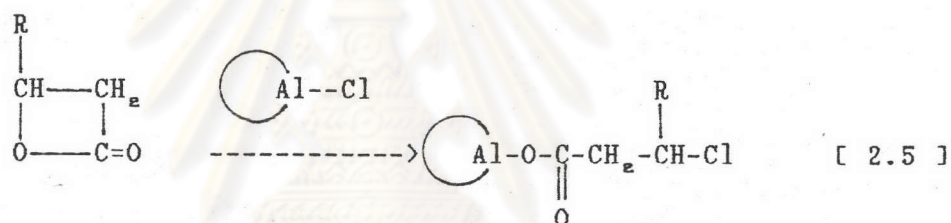
The pivalolactone, α,α -dimethyl- β -propiolactone, is remarkably easy to be polymerized by anionic ring-opening polymerization. The reaction takes place rapidly and completely in organic media at mild temperatures. Early studies on pivalolactone (34) establish that its polymerization is initiated by tertiary amines and phosphines. The reaction was visualized as occurring in following two steps.



There are initiators for polymerizing of lactones such as cyclic amine (35), $\text{AlEt}_3/\text{H}_2\text{O}$ and $\text{ZnEt}_2/\text{H}_2\text{O}$ (36), aluminium porphyrin and its derivatives (37,38) and μ -oxo-bime-

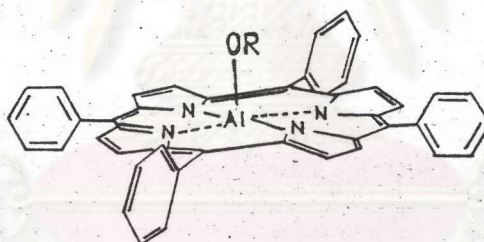
tallic trinuclear alkoxides (39).

Inoue and Aida (37) found that ring-opening of β -lactone by tetraphenylporphinato aluminum chloride (TPPAlCl) preferably takes place at the alkyl-oxygen bond (Equa. 2.5). The phenomenon is confirmed by an observed strong absorption band of carboxylate group at 1600 cm^{-1} and a triplet signal at -0.7 ppm ($^1\text{H-NMR}$) from protons of the methylene group of a porphinatoaluminum carboxylate.



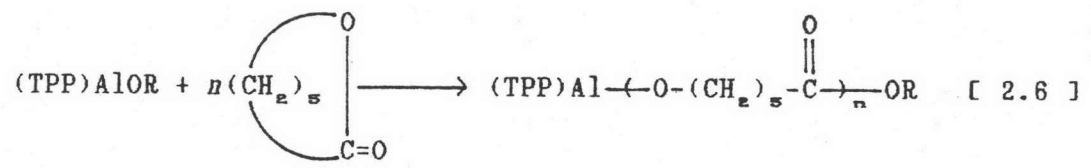
The most important polymer obtained from the ring-opening polymerization of lactones is poly(ϵ -caprolactone) (PCL). Many initiators (sometimes called catalysts) are used to initiate the ring-opening polymerization of ϵ -caprolactone (ϵ -CL). Cox, et al. reported that the ring-opening of ϵ -CL was initiated by di-n-butylzinc and underwent polymerization in anhydrous toluene, at 80°C , and under nitrogen atmosphere. Pitt, et al. (40) found that the polymerizations of ϵ -CL which are performed in bulk systems and initiated with stannous octoate at different temperatures and reaction times, are characterized by rapid initiation, invariance of the number of growing chains corresponding to the amount of initiator, and a dominant role played by

ester interchange reactions. Morton and Wu (41) reported that rapid polymerizations and high molecular weights are obtained the ring-opening of ϵ -CL initiated with butyllithium and lithium t-butoxide in tetrahydrofuran and benzene solvents, at 25 ° C. Inoue, et al. (42) found that (5, 10, 15, 20-tetra-phenylporphinato) aluminum alkoxide-alcohol system { (TPP) AlOR } is an excellent initiator for the polymerization of ϵ -CL to give the corresponding polyester having a narrow molecular weight distribution.



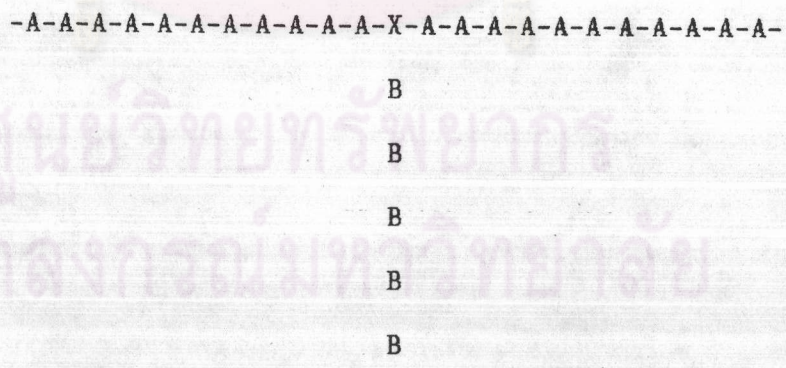
(TPP) AlOR

However, the molecular weight of obtained polymers was quite low (< 30,000) and the reaction of that system had another disadvantage for taking a long time. The polymerization of ϵ -CL initiated with (TPP) AlOR is represented by Equation 2.6.



2.2 Graft copolymerization

The graft copolymerization is a method for synthesizing a so called " graft copolymer " comprising molecules with one or more species of block connected to the main chain as side chains having constitutional or configurational features that differ from those in the main chain, exclusive of branch points. The simplest case of a graft copolymer can be represented by the structure below;



Scheme 2.1 The representation of graft copolymer; (A) is the repeating unit of the main chain, (B) is of the side chain and (X) is the branch point.

where a sequence of A monomer units is referred to as the main chain or backbone, the sequence of B units is the side chain or graft, and X is represented for the units in the backbone to which the grafted chains are attached. In graft copolymers the backbone and the side chains may both be homopolymeric, the backbone may be homopolymeric and the side chains copolymeric or vice versa, or both backbone and side chains may be copolymeric but of different chemical compositions.

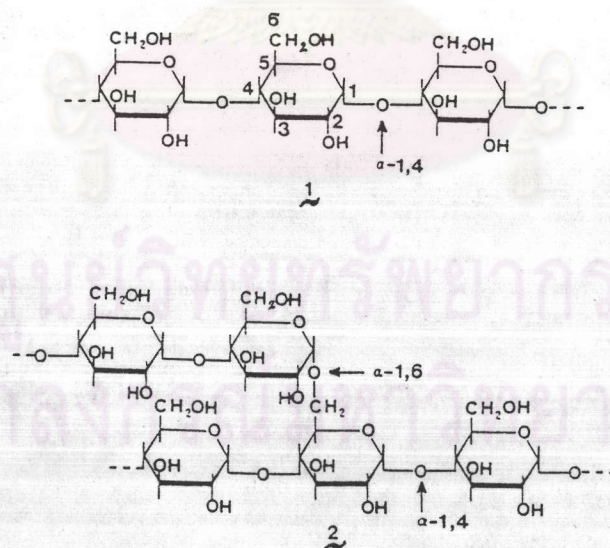
Because the main chain and the branches are usually thermodynamically incompatible, thus most graft copolymers can be classified as multiphase polymers in the solid state. Free radical polymerization methods are the oldest and most widely used for the synthesis of graft copolymers since they are very simple and relatively practical (43). However, they usually give heterogeneous materials that are difficult to characterize.

2.2.1 Starch as a raw material

Starch (44, 45), the principle reserved polysaccharide in plants, constitutes a substantial portion of the human diet. It is commonly known that starches are stored in many parts of plants such as seeds, fruits, tubers, roots, stem pith, etc, and are produced commercially from corn, wheat, rice, tapioca, potato, sago, and other sources. Corn starch is the most important starches manufactured in the United States. Starch of excellent quality can be prepared from white potatoes.

Starches from other sources (cassava, tapioca, etc) are prepared in a manner similar to that for corn or potato starch.

Starch (46) is composed of two polysaccharides; amylose and amylopectin, both polymers consisting of linked D-anhydro-glucose residues. In amylose [1] the residues are joined by α -1,4-linkages to give a linear polymer. In the large branched amylopectin [2], side chains are grafted to the linear α -1,4-polymer by a single α -1,6-linkage at intervals of 20 units or so. These branches occur in clusters like the string elements of a tassel. This unique branch is referred to as a racesome structure.



Scheme 2.2 The structures of amylose and amylopectin

Natural starches occur in a number of different polymorphic forms. The cereal starches give an X-ray pattern classed as " A ", and the starches of tubers yield a " B " pattern. The most probable mode for crystallization of starches is double helix and that the uniquely shaped amylopectin molecule, with its clusters of short branches, is the predominant crystalline component. Indeed, starches composed solely of amylopectin crystalline as well as or better than those containing amylose. The presence of water favors starch crystallinity, with both "A" and " B " structures being interpreted in terms of hydrates.

The size of starch granules may vary from 2 to 150 μ m. Rice starch has the smallest granules and potato the largest. Microscopic examination of starch granules reveals a distinct cleft call hilum, the botanical center of the granule, ie, it is the nucleus around which granule growth occurred.

Undamaged starch granules are insoluble in cold water but imbibe water reversibly and swell slightly. However, in hot water a large irreversible swelling occurs producing gelatinization which takes over at discrete temperature range that depends on types of starches as shown in Table 2.1.

Table 2.1 The temperature ranges for starch gelatinization

<u>Starch</u>	<u>Range, °C</u>
potato	59-68
tapioca	58.5-70
corn	62-72
waxy corn	63-72
wheat	58-64

At a certain temperature in the heating process (the lower limit of the gelatinization temperature), the kinetic energy of the system is sufficient to overcome the hydrogen bonding in the interior of the starch granule. The amorphous regions of the granule are solvated first and the granule swells rapidly, eventually to many times its original size. During swelling, and as a consequence of it, some of the linear amylose molecules are leached out of the granule into solution. The gelatinization temperature is the range between the lower limit, indicating onset of granule swelling, and the upper limit, corresponding to the point where almost all granules are 100 % gelatinized. The gelatinization range depends upon the methods used to measure it. The most sensitive method follows microscopically the loss of birefringence of a starch slurry heated on a Kofler hot stage. Other chemicals present in the slurry may affect the gelatinization range in a predictable way, and this information

may be important to certain industrial applications of starch. Certain chemicals, such as sodium sulfate, sucrose, and dextrose, inhibit gelatinization and increase the gelatinization temperature, probably by competing for available water. Other chemicals such as sodium nitrate, alkali, and urea, lower the gelatinization temperature range, possibly by disrupting granular intermolecular hydrogen bonds.

2.2.2 Polysaccharide graft copolymers

Polysaccharides are the naturally occurring polymers or biopolymers obtained from biosynthesis of the corresponding saccharide units during the progressing anabolism. The well-known polysaccharides are cellulose, starch, and their complexing derivatives such as cotton, wood pulp, and fiber. Polysaccharides are degraded easily as they are important carbon and energy sources for most organisms. The enzymatic catalysis can undergo either inside or outside organism cells.

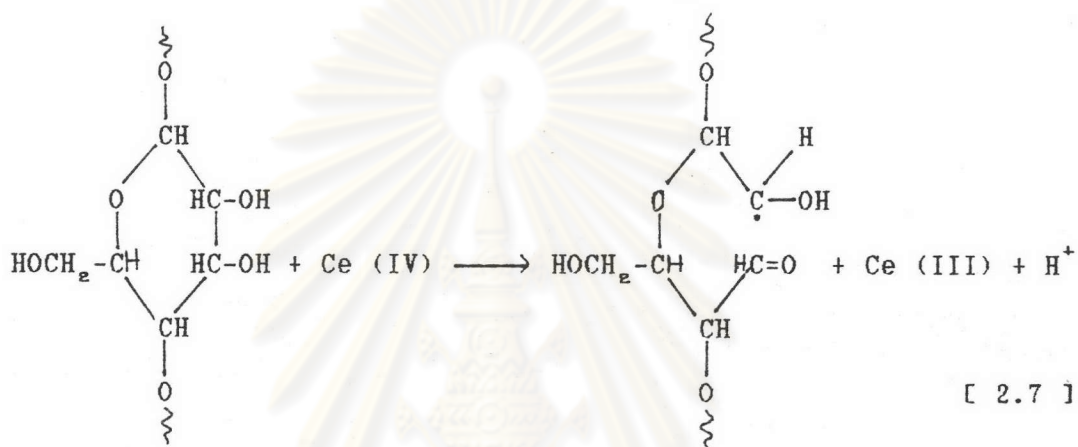
The graft copolymerizations of various vinyl monomers onto polysaccharides have been studied actively and widely in order to get more applicable materials. The modified starch prepared by Mn (III) initiated grafting of acrylonitrile onto starch, absorbed water vapor like other polysaccharides at relative humidities (RH) up to 95-97 %. At higher RH the water vapor absorption was increased quickly. In contact with liquid distilled water the modified starch became superabsorbent

by retaining very large amounts of water (up to 800 g/g) (47). The graft copolymerization of acrylonitrile onto starches carried out in the presence of ceric ammonium nitrate as an initiator gave graft copolymers which were converted into water-water absorbents by saponification or alkali-hydrolysis (48-51). The graft copolymerization of vinyl monomers have been developed by using Mn(III) ion dissolved in aqueous solution as an initiator. The Mn(III) grafting method has been applied as an efficient process for preparation of water retaining materials (52).

Polyacrylic acid-cellulose grafts were considered as ion-exchange materials because they had capacities available for ion-exchange and the rate of ion-exchange was quite rapid enough for using in such an application (53).

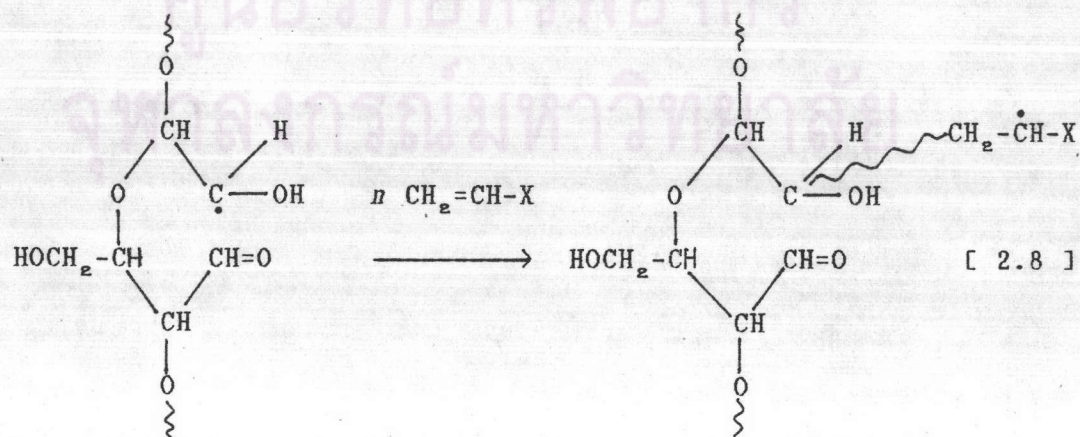
The various initiators and monomers were used in the synthesis of starch-based graft copolymers. Polystyrene was grafted onto starch and cellulose by a simple method that involves heating semisolid mixtures composed of polysaccharides, styrene, and an aqueous solution of potassium persulfate (54). The linear fraction of starch (amylose) could be used to prepare graft copolymers having polymethyl methacrylate (55) and polybutyl acrylate (56) as side chains. Some of the starch graft copolymers were investigated their biodegradability and found they were potentially biodegradable. Graft copolymerization of polysaccharides are initiated with various types of initiators (57) and among them, the ceric ion initiator is the

most promising and practical one. It is believed that grafting of vinyl monomer onto cellulose and starch occurs via free-radical reactions. The reaction occurs firstly by radical production;

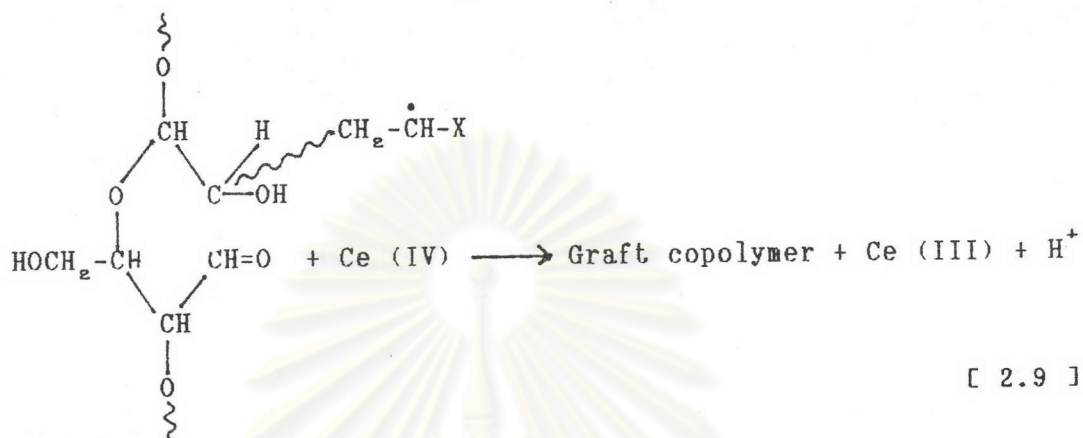


The initiation of grafting and other reaction follows;

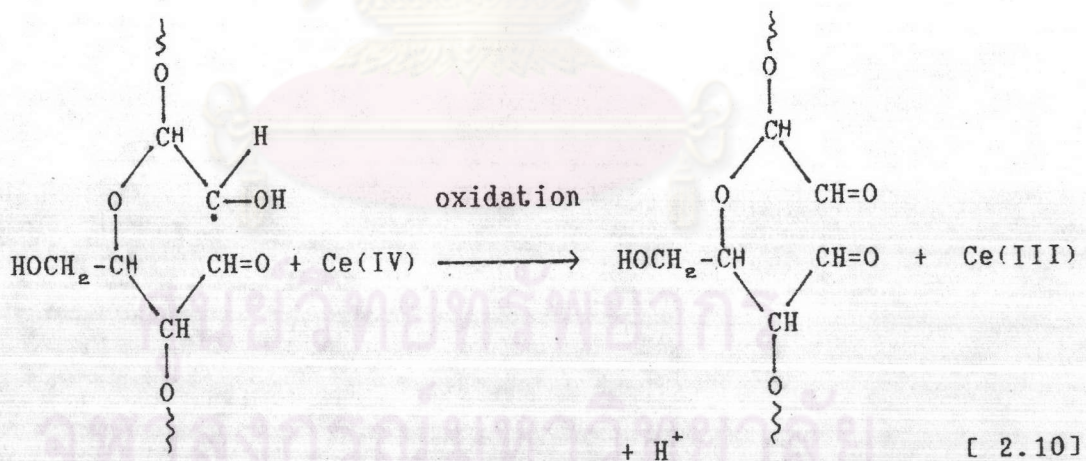
Grafting initiation



Grafting termination: Termination is mostly caused by ceric ion.



Oxidation: The radical may suffer simultaneous oxidation.

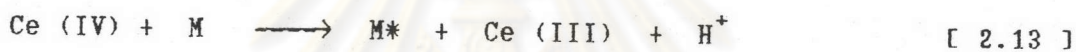
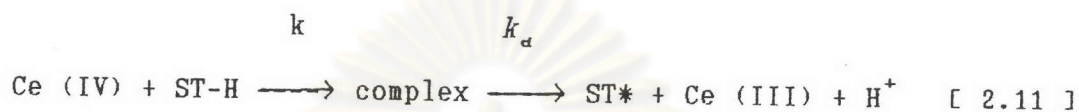


2.2.3 The mechanism of grafting copolymerization

The mechanism of grafting suggested by Samal, et al. (57) is reasonably plausible for the reaction of cellulose. Mahmood, et al. (58) also postulated the mechanism of graft

copolymerization onto jute fiber initiated by ceric ion. These two mechanisms are similar. The mechanism of starch graft copolymerization is supposed to be similar to that of cellulose.

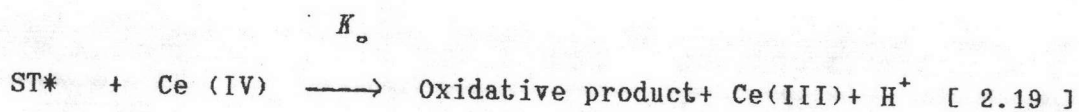
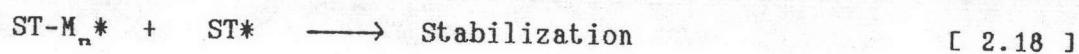
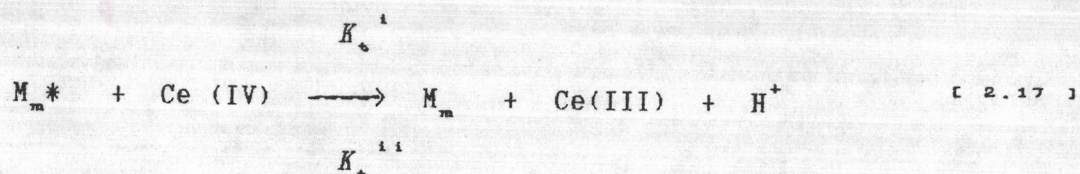
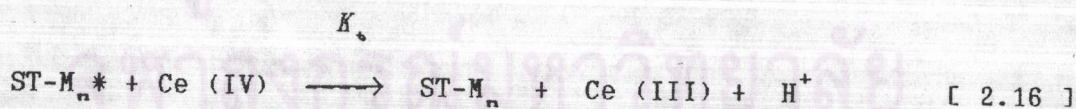
Initiation:



Propagation:



Termination:



where ST-H denotes a reactive group in starch, M is a monomer, K is the equilibrium constant, and k_1 , k_1' , k_p , k_p' , k_t , k_t' , and K_0 are rate constants.

Step [2.11], an equilibrium step, may represent the adsorption of Ce (IV) on starch and then followed by the decomposition of starch-Ce (IV) complex to give active free-radical on starch. The presence of monomer may initiate step [2.12]. The monomer may be initiated directly by Ce (IV) to give monomeric free-radical in step [2.13]. The growing of side chains is in step [2.14] and is terminated by Ce (IV) in step [2.16] and by ST in step [2.18]. Grafting is affected when step [2.12] becomes unfavourable and step [2.13], which is the initiation of homopolymerization, is predominant. The predominant steps [2.12] and [2.14] are essentially required for good yield of grafting reaction.

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