CHAPTER II

THEORY AND LITERATURE SURVEY

2.1 SILK

Silk, the only natural continuous filament fibre, is a protein composed of fibroin, the true fibre portion, and sericin, the natural gum or size which coats the fibroin as it is extruded by the silkworm.

Silk is used to denote the fibroin obtained from the species *Bombyx mori*. It is classified as a polypeptide and is composed primarily of four amino acids: glycine, alanine, serine and tyrosine as shown in Table 2.1 [1]. Therefore, fibroin molecules have more hydroxyl groups than amino groups of basic amino acid in arginine and lysine and less carboxyl groups of acidic amino acid in aspartic acid and glutamic acid. Table 2.2 depicts the chemical structure and the relevant molecular weight of the amino acids contained in silk fibres [2].

TABLE 2.1 Amino acid compositions of fibroin (Bombyx mori)

(gm/protein 100 gm)

Amino acid		Fibroin
Nonpolar amino acid	Glycine	41.25
	Alanine	28.87
	Valine	2.63
	Leucine	0.32
	Isoleucine	0.44
	Phenylalanine	0.55
Acidic amino acid	Aspartic acid	0.76
	Glutamic acid	0.69
Basic amino acid	Arginine	0.56
	Lysine	0.17
Oxy amino acid	Serine	13.22
	Threonine	0.81
	Tyrosine	10.96

TABLE 2.2 Structural formulae of the main amino acids contained in fibroin

Name	Formula	Molecular weight
Glycine	HOOC-CH_2 with NH_2	75
Alanine	HOOC-CH-CH_3 with NH_2	89
Serine	$\text{HOOC-CH-CH}_2\text{-OH}$ with NH_2	105
Tyrosine	HOOC-CH-CH_2⟨○⟩-OH with NH_2	181

Silk contains no disulfide crosslinks. It is a highly crystalline material with hydrogen, hydroxyl and various salt linkages all of which make it non-thermoplastic. The general form of polypeptide chain of silk is shown below:

$$-CO-NH-\underset{|}{\overset{R_1}{CH}}-CO-NH-\underset{|}{\overset{R_2}{CH}}-CO-NH-\underset{|}{\overset{R_3}{CH}}-$$
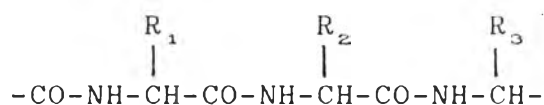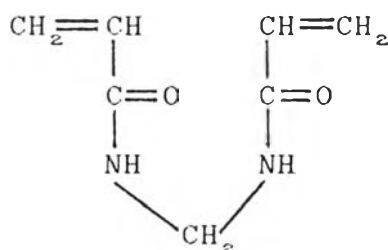
The importance of silk as a textile fibre lies in its soft and deep lustre, handle, draping qualities and luxurious appearance. Silk is comfortable to wear because it is so absorbent. It dries quickly and gives up soil easily due to its smooth surface. Although silk is reasonable resistant to diluted mineral acids, and is usually dyed with acid dyes or with direct dyes from a neutral salt solution, it is attacked by strong acid which thus renders it dissoluble in such solution.

Silk has a high elastic modulus with a limited though useful extensibility but high strength both when dry and wet, mainly due to its peculiar microstructural characteristics such as crystallinity, strong hydrogen bonds between the $C=O$ and $-NH$ groups of adjacent molecules and amorphous regions showing a high crystalline order and composed of bulky side chain. However, the silk fibre displays a low light resistance and low wrinkle recovery which can be improved by modifying its properties through graft copolymerization [3].

2.2 N,N'-METHYLENEBISACRYLAMIDE

N,N'-methylenebisacrylamide or N,N'-MBA whose structure shown below is a crystalline powder is often used as a crosslinking agent in graft copolymerization to

increase the quality of naturally occurring fibres. The appreciable dyeability effect of N,N'-MBA on natural fibres has prompted investigation of grafting of this monomer onto silk fibres in the presence of metal chelate, where the monomer facilitates the production of free radicals by enhancing the homolytic cleavage of M-O bond [4]. It is a non-conjugated divinyl monomer with the following structure

$$CH_2=CH \qquad CH=CH_2$$
$$|\qquad\qquad\qquad|$$
$$C=O \qquad\quad C=O$$
$$|\qquad\qquad\qquad|$$
$$NH \qquad\qquad NH$$
$$\diagdown \qquad\qquad \diagup$$
$$CH_2$$

which gives rise to crosslinked insoluble polymer and yields a soluble, gel-free polymer accordingly [5].

2.3 GRAFT COPOLYMERIZATION

Modification of fibres such as silk, wool, cellulose, jute and rayon via graft copolymerization with vinyl monomer has been the subject of much interest and has provided a potential route for significantly altering the physical and mechanical properties.

The synthesis of a graft copolymer requires the formation of a reactive centre on a polymer molecule in the presence of a polymerizable monomer.

It is important to graft copolymerize onto fibres with maximum percentage grafting but minimum homopolymer. The higher the grafting, the better properties of the grafted fibres, as indicated by Kobayashi et al.[6]. They observed that the wrinkle recovery of the MMA-grafted silk fibres increased when the graft yield was in the range of 30-60%. The formation of homopolymer on the fibre surface usually destroys the basic properties of fibres.
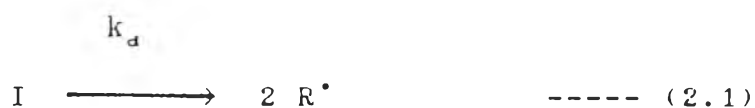
Most methods of synthesizing graft copolymers involve the use of free-radical chain polymerization rather than ionic chain polymerization because of the reaction conditions and ease of carrying out the reaction.
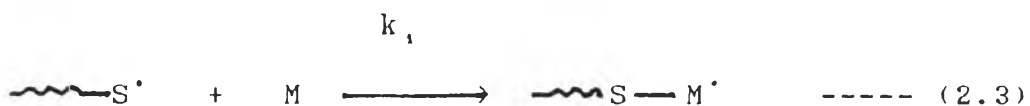
2.3.1 Free-radical Graft Copolymerization

Radical chain polymerization is a chain reaction consisting of a sequence of steps as follows: (1) *an initiation step*, which may involve more than one reaction; (2) *a propagation step*, which involve a long sequence of identically repeating reactions; and (3)

a *termination step,* which ends the kinetic chain reaction. The example of reaction mechanism of graft copolymerization onto silk fibre is shown below [7]:
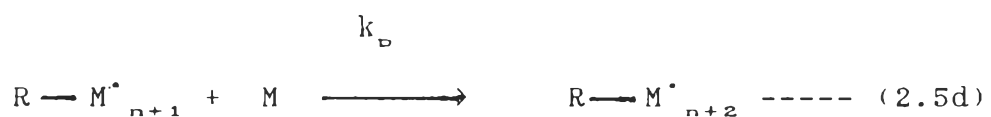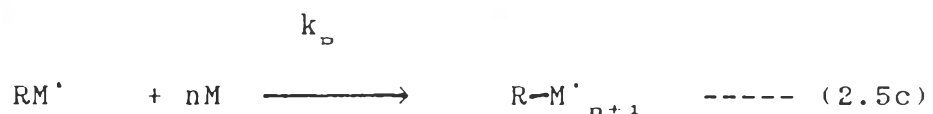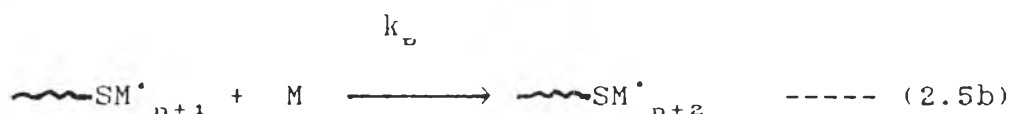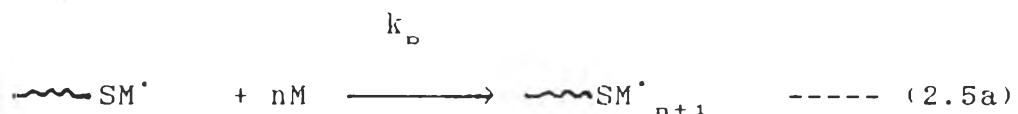
Production of free radicals on the silk backbone:

$$I \xrightarrow{k_d} 2 R^\bullet \qquad ----- \quad (2.1)$$

$$\text{\textasciitilde{}SH} + R^\bullet \xrightarrow{k_{tr}} \text{\textasciitilde{}S} + RH \qquad ----- \quad (2.2)$$

Initiation:

$$\text{\textasciitilde{}S}^\bullet + M \xrightarrow{k_i} \text{\textasciitilde{}S} - M^\bullet \qquad ----- \quad (2.3)$$

$$R^\bullet + M \longrightarrow RM^\bullet \qquad ----- \quad (2.4)$$

Propagation:

$$\text{\textasciitilde{}SM}^\bullet + nM \xrightarrow{k_p} \text{\textasciitilde{}SM}^\bullet_{n+1} \qquad ----- \quad (2.5a)$$

$$\text{\textasciitilde{}SM}^\bullet_{n+1} + M \xrightarrow{k_p} \text{\textasciitilde{}SM}^\bullet_{n+2} \qquad ----- \quad (2.5b)$$

$$RM^\bullet + nM \xrightarrow{k_p} R\text{--}M^\bullet_{n+1} \qquad ----- \quad (2.5c)$$

$$R - M^\bullet_{n+1} + M \xrightarrow{k_p} R\text{--}M^\bullet_{n+2} \qquad ----- \quad (2.5d)$$

Termination:

$$\text{\small\wedge\wedge}SM^{\cdot}_{n+2} \ + \ M^{\cdot}_{m}S \ \xrightarrow{k_t} \ \text{Grafted polymer} \quad \text{---} \ (2.6a)$$

$$R\text{---}M^{\cdot}_{n+2} \ + \ M^{\cdot}_{m} \ \xrightarrow{k_t} \ \text{Homopolymer} \quad \text{---} \ (2.6b)$$
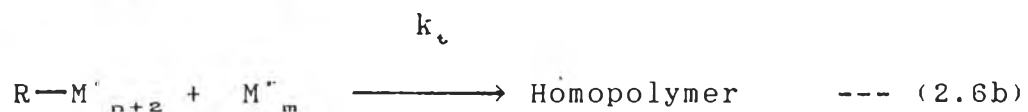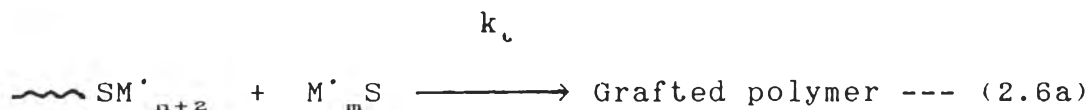
2.4 INITIATION

Radicals can be produced by a variety of redox, thermal, and irradiation methods. In order to function as a useful source of radicals, an initiator system should be readily available, stable under ambient or refrigerated conditions, and possess a practical rate of radical generation at temperatures which are not excessive (approximately $<150^{\circ}$C) [8].

2.4.1 Redox Initiation

Redox initiation is often an efficient method of initiating graft polymerization. It usually results in grafting with a minimum of homopolymerization since only the polymeric radical is formed.

A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperatures, depending on the particular

redox system, including initiation at moderate temperatures of $0-50^{\circ}C$ and even lower [8].

Some redox systems involve direct electron transfer between reductant and oxidant, while others involve the intermediate formation of reductant-oxidant complexes; the latter are charge transfer complexes in some cases [8].

2.4.1.1 Types of Redox Initiator

2.4.1.1.1 Peroxides in combination with a reducing agent are common sources of radicals, for example,

$$H_2O_2 + Fe^{2+} \longrightarrow HO^- + HO^{\cdot} + Fe^{3+} \quad --- \quad (2.7)$$
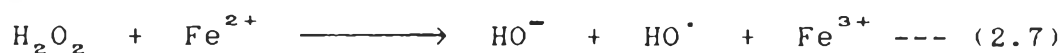
2.4.1.1.2 The combination of a variety of inorganic oxidants initiates radical polymerization, for example,

$$^-O_3S-O-O-SO_3^- + Fe^{2+} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-\cdot} \quad -- \quad (2.8)$$

2.4.1.1.3 Organic - inorganic redox pairs can also initiate polymerization, usually but not always by oxidation of the organic component, for example,

$$R-CH_2-OH \; + \; Ce^{4+} \; \longrightarrow \; Ce^{3+} \; + \; H^+ \; + \; R-\overset{\bullet}{C}H-CH \; -- \; (2.9)$$
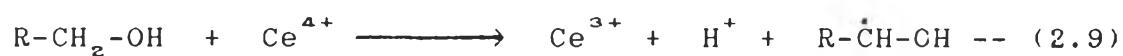
Other redox pairs include transition metal chelates.

2.4.2 Thermal Decomposition and Mechanical Degradation

Thermal decomposition is the method which may be used to initiate graft copolymerization by the decomposition of thermally unstable groups on a polymeric backbone [9].

Mechanical degradation or *Mastication* [9] is the method which leads to the formation of macroradicals capable of initiating graft copolymerization under the influence of an applied stress scission of the carbon-carbon or other chemical bonds between atoms within the backbone of a polymer macromolecule.

2.4.3 Ionizing Radiation

Polymeric radicals can alternately be produced by the irradiation of a polymer-monomer system with ionizing radiation. Radiation is a very convenient source for graft initiation as it allows a considerable degree of control to be exercised over structural factors

such as the number and length of the grafted chain by careful selection of the dose and dose-rate. *Preirradiation* and *mutual irradiation* are two different techniques used for radiation grafting [8,9].

2.4.4 Ultraviolet Radiation

Graft copolymerization can also be achieved by irradiation of a polymer-monomer system with ultraviolet radiation, often in the presence of photosensitizer such as benzophenone or benzoin. Photolytic grafting is similar to radiation grafting except that the depth of penetration by UV is less than by ionizing radiation. UV-initiated grafting is generally limited to surface modification of a polymer [8,9].

2.4.5 Chain Transfer and Copolymerization

An active site capable of initiating graft copolymerization may be formed on a polymer via a "chain transfer" step in vinyl addition polymerization. For initiation by chain transfer, the efficiency of the grafting reaction is dependent on the tendency of a propagating radical to transfer to polymer compared to propagation [10].

2.5 METAL CHELATES

Metal chelates are compounds containing donor atoms that can combine by coordinate bonding within a single metal atom to form a cyclic structure called a chelation complex or, simply, a chelate.

The structural essentials of a chelate are coordinate bonds between a metal atom and two or more atoms in the molecule of the chelating agent. The coordinating atoms of the ligands are electron donors and the metal atom is the electron acceptor [11].
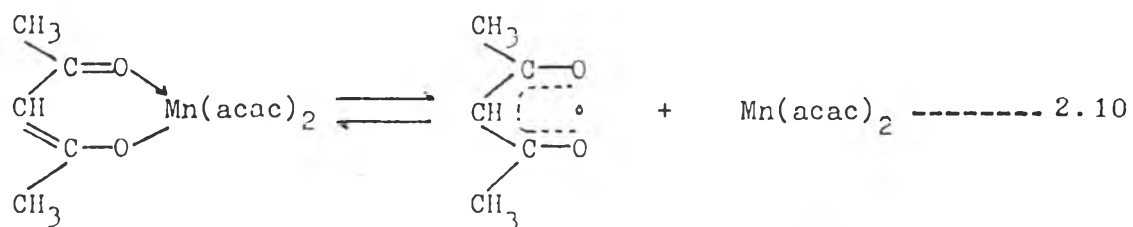
Metal chelates have many applications and the one which is very important to polymerization or graft copolymerization is being the initiator. Most of them usually are concerned in redox initiation. When a metal is capable of existing in more than one valency state, the combination of an organic ligand with the higher valency state of the metal may result in an electron transfer to the metal and the initiation of a chemical reaction as a consequence of this electron transfer; in other words, the chelates containing the metal in the higher valency state are always more active [12]. In other catalytic effects of metal chelates, reactive centers may be brought into close

proximity, charge or bond strain effects may be created, or elecron transfer may be made possible [11].

Metal chelates have been reported to produce free radical species upon heating and these species were found to effect the polymerization of styrene. Following this finding, a number of workers attempted the polymerization of a variety of vinyl monomers by using metal chelates as initiators.

The use of metal chelates for initiating vinyl polymerization has attracted attention in recent years. The initiating activities of acetylacetonate complexes of some metals(Me(acac)$_x$) -such as Mo(II), Mo(III), Fe(III),Cr(III), Co(III), and Mn(III)- which involve the central metals of higher valency state are known as excellent initiators of vinyl polymerization [13].

Arnett and Mendelsohn [14] observed that metal chelates, upon heating, decompose to generate free radical species by homolysis of metal-oxygen bond with the reduction of the metal to a lower valency state as shown in eqn. 2.10

$$\begin{array}{c} CH_3 \\ C=O \\ CH \qquad Mn(acac)_2 \\ C-O \\ CH_3 \end{array} \rightleftharpoons \begin{array}{c} CH_3 \\ C-O \\ CH \qquad \cdot \\ C-O \\ CH_3 \end{array} + \quad Mn(acac)_2 \quad \text{-------- 2.10}$$

The monomer molecule must participate in the homolysis of $Me(acac)_x$, i.e., in the initiating radical production step in equation 2.11

$$Me(acac)_x + M \rightleftharpoons [M \longrightarrow Me(acac)_x]$$

$$(acac)_x - M^. + Me(acac)_{x-1} \qquad \text{------(2.11)}$$
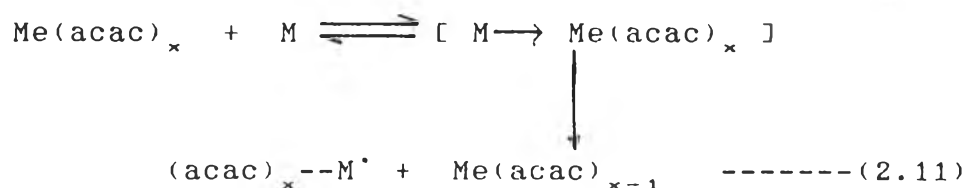
2.5.1 Manganese(III) Acetylacetonate

Kastning et al. [15] showed that with various chelates of Mn(III), the acetylacetonate is considerably more active than dibenzoylmethane derivatives, those of Mn(III) and Co(III) are the most active initiators as shown in Figure 2.1.
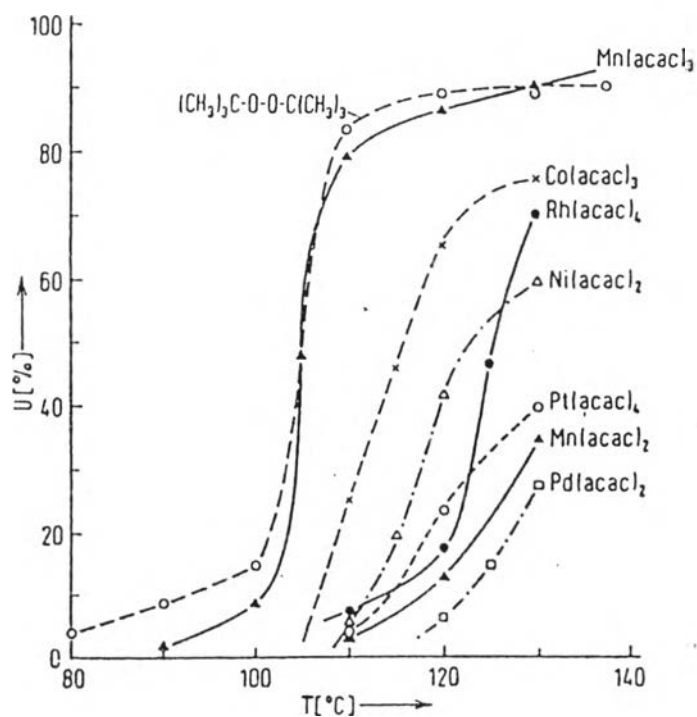
FIGURE 2.1   Polymerization of styrene using metal

acetylacetonates as initiators. The

percentage of conversion (U) as a

function of the temperature (T).

acac = Acetylacetonyl.   (Duration of

polymerization 1 hour, initiator

concentration 0.5 wt%).

Otsu et al. [16] found that Mn(acac)$_3$ was the most effective initiator, and Co(acac)$_3$, Mn(acac)$_2$, Cu(acac)$_2$ and Cr(acac)$_3$ gave moderate activity for the polymerization of methylmethacrylate at 80°C, as shown in Table 2.3.

TABLE 2.3 Results of bulk polymerization of MMA initiated by Me(acac)$_x$ at 80°C: [Me(acac)$_x$] = 0.53 to MMA

Me in Me(acac)$_x$	Time, hr	Conversion, %	Rp, % /hr	Syndiotacticity, %
Mn(III)	0.5	15.11	30.22	39
Co(III)	1.5	4.82	3.21	43
Mn(II)	1.5	4.25	2.83	53
Cu(II)	2.0	4.64	2.32	48
Cr(III)	2.0	5.61	2.24	-
Al(III)	8.0	2.89	0.36	-
Ni(II)	10.0	1.82	0.18	46
Fe(III)	11.0	3.87	0.35	47
Co(II)	11.0	3.53	0.32	42
TiO(II)	11.0	2.88	0.26	41
Zr(IV)	11.0	2.18	0.20	42
Zn(II)	11.5	2.56	0.22	-
VO(II)	20.0	2.48	0.12	-
Li(I)	20.0	1.87	0.09	-
Na(I)	20.0	0.66	0.03	-
Mg(II)	30.0	3.28	0.11	-
V(III)	30.0	0.15	0	-
MoO$_2$(II)	30.3	0.13	0	-

The observed activity order of Me(acac)$_x$ was independent of their stability constant (in water), thermal stabilities, ionization potentials or electronegativities of their central metals.

The abnormally high initiator activity of Mn(acac)$_3$ might be based on its structural strain [15].

2.6   FACTORS INFLUENCING THE PERCENTAGE GRAFT COPOLYMERIZATION

There are several influencing parameters imposing degree of graft copolymerization; however, the most important ones are listed below.

2.6.1   Initiator

The variation of grafting efficiency or % conversion in graft copolymerization or polymerization depends to a certain level on the *initiator effect*. Smets et al. [17] have shown that the polymerization of methyl methacrylate in the presence of polystyrene yields an appreciable amount of graft copolymer if the reaction is initiated with benzoyl peroxide. In contrast, when using azo-bis-isobutyronitrile (AIBN) or di- *tert*- butyl peroxide as an initiator the degree of grafting is insignificant. The explanation for the inability of AIBN to initiate graft

copolymerization is that the $(CH_3)_2C-CN$ radical from AIBN is appreciably less reactive than the C_6H_5 and $C_6H_5COO^\cdot$ radicals from benzoyl peroxide because of the resonance stabilization.

Bamford and Lind [18] studied how $Mn(acac)_3$ was relatively effective with MMA at $80^\circ C$ and vinyl acetate but ineffective with acrylonitrile. In addition, they also examined the influence of substituents in the acetyl-acetonate ligand. Manganese 1,1,1-trifluoroacetylacetonate, $(Mn(facac)_3)$, initiates the polymerization of methyl methacrylate and acrylonitrile rapidly, but is inactive toward styrene and vinyl acetate; thus it is a good initiator for monomer structures susceptible to anionic polymerization, although the actual propagation pathway is by free radical. Initiation by $Mn(facac)_3$ is more effective with acrylonitrile compared to $Mn(acac)_3$. This implies that the central carbon atom of the radical, $CH_3CO\overset{\cdot}{C}HCOCH_3$, carries a partial positive charge, so that reaction with acrylonitrile will be relatively slow; on the other hand, initiation by $Mn(facac)_3$, having some ionic character, can be very rapid [18,19].

The graft yield increased with increasing initiator concentration, but thereafter the percentage of grafting decreased appreciably due to retardation or

inhibition by the initiator (the chelates) which occurred at the higher concentration [18]. $Mn(acac)_3$ is known to act as retarder of vinyl polymerization at higher concentration[20]. The retardation in graft reaction is presumably due to the oxidation of the polymer backbone radical and the variation in ratio between monomer and chelates. In addition, the exceedingly free radicals formed at high concentrations of initiator, the termination of free radicals also occurred [7].

2.6.2 Monomer

Vinyl monomers which are able to graft copolymerize by using metal chelates as initiators should have a functional group which increases the π-electron density of the double bond.

S. Samal and G. Sahu [21-23] studied the effect of various monomers on graft yield. MMA was found to be the most active vinyl monomer, the order of reactivity being methyl methacrylate > methyl acrylate > ethyl acrylate > n-butyl acrylate > acrylonitrile > acrylic acid. This order of reactivity suggests that the formation of initiating radical is of monomer dependence, leading to the formation of an intermediate complex. The ease of formation of such a complex will be maximum with MMA
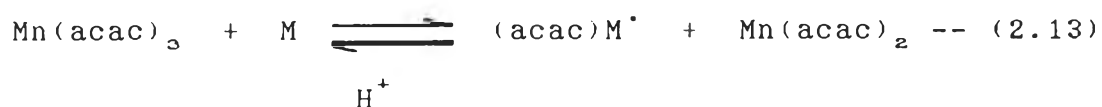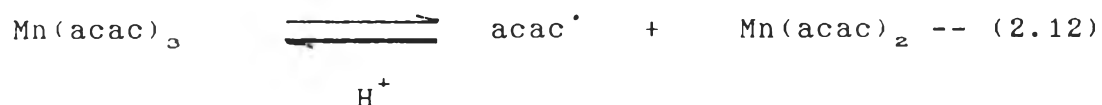
because of the increased π-electron density due to +I effect of the substituted methyl group. In case of AN and AA, the $-\overset{|}{\underset{|}{C}}N$ and -COOH groups significantly decrease the π-electron density due to an electron attracting group attached to the vinylic carbon atom, leading to a decreased reactivity forming a complex with the chelate. The decrease in graft yield from MA to BA is largely due to steric hindrance. The approach of the monomer to form charge transfer complex with the initiator is sterically hindered.

Structure of monomer, indeed, plays an important role in graft yield due to the fact that the rate of initiation is determined by the ease facility with which the monomer enters into the metal chelate to form a charge transfer complex [18].

By increasing the monomer concentration, the graft yield increased. However, at higher concentration of the monomer, the rate of combination and disproportionation of PMMA macroradicals is increased faster than the rate of their combination with the polymer backbone. Besides, the rate of monomer diffusion is bound to be progressively affected by the polymer deposit formed, and this is more pronounced at higher concentration of monomer [22].

2.6.3 Acidity

To graft copolymerize the vinyl monomer onto silk fibres by manganese(III) acetylacetonate as an inititor, it is necessary to start the reaction in an acidic medium with appropriate concentration. Acid facilitates the decomposition of the initiator, leading to the formation of a large number of initiating free radicals. Incorporating too high of a concentration of the acid should be avoided because it does suppress the generation of radicals due to the reversible reaction which scavenges the existing radicals [21].

$$Mn(acac)_3 \underset{H^+}{\overset{}{\rightleftharpoons}} acac^{\bullet} + Mn(acac)_2 \quad -- \ (2.12)$$

$$Mn(acac)_3 + M \underset{H^+}{\overset{}{\rightleftharpoons}} (acac)M^{\bullet} + Mn(acac)_2 \quad -- \ (2.13)$$

2.6.4 Temperature

In graft copolymerization by the metal acetylacetonate with increasing temperature within the range of $45°C-75°C$, the graft yield increases. This can be ascribed to: (a) greater ease of acetylacetonate free radicals formation; (b) increased solubility; and (c) enhanced diffusion rate of monomer molecules to the vicinity of the
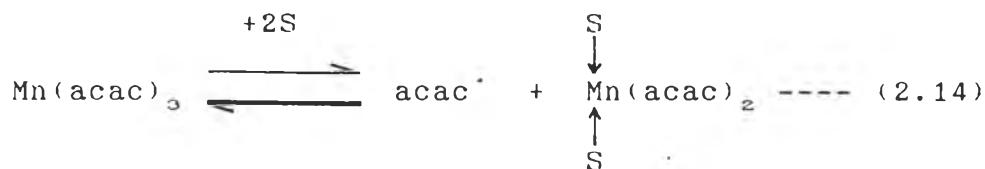
growing macroradicals. However, at higher temperature, it appears that termination reactions are also accelerated leading to a decrease in percent add-on.

2.6.5 Time

The percentage grafting on variation of the reaction periods was studied. The results show that with an increase in the reaction period, the percentage grafting increases.

2.6.6 Additives

The formation of acetylacetonate free radical is assisted by the solvent and monomer. Bamford et al. [18] suggested that if the solvent molecules were a polar solvent, they probably encourage the decomposition of the chelate by stabilizing the divalent chelate generated in the process

$$Mn(acac)_3 \;\underset{}{\overset{+2S}{\rightleftharpoons}}\; acac^{\cdot} \;+\; \overset{\displaystyle S}{\underset{\displaystyle S}{Mn(acac)_2}} \;----\; (2.14)$$

Organic solvents greatly affect the graft yield. The effect of different types of solvents such as alcoholic solvents, chain transfer solvents, organic acid and solvents acting as solubilizers for the monomers is discussed below.

With alcoholic solvents the graft yield follows the order: MeOH > EtOH > n-Pr-OH > n-butyl-OH > amyl alcohol. It was shown that in increasing the molecular weight of the alcohol, graft yield decreased due to the adverse effect of the water on the swelling of silk. The hydrophobic character of the solvent increases from methanol to amyl alcohol, thereby hindering monomer access to reactive sites on the silk.

With chain transfer solvents, the graft yield order is $CHCl_3$ > CCl_4 > EtSH.

With other solvents, the graft yield order is formic acid > acetic acid > acetone > DMF > dioxane. Besides, DMF, DMSO and pyridine appear to act as chain transfer solvents which deactivate the active sites of backbone polymer [22].

Regardless of the solvent used, an increase in the amount of solvent in the reaction mixture tends to decrease graft yield. This might be due to the fact that at higher concentration, the solvents act as chain terminator [4,24].

Dependence of grafting upon the nature of the solvent suggests that the solvents examined behave

considerably differently in their: (a) compatibility of swelling silk; (b) miscibiliity with monomer; (c) formation of solvent radical from the primary radical species of the initiating system; (d) contribution of the solvent radical in the activitation of the silk; (e) increased concentration of the initiating free radical by assisting the degradation of the chelate, and termination of the graft radical and silk macroradical via chain transfer. Situations a-d are factors favoring grafting by simplifying access and diffusion of the monomer; but situation (e) is the only factor lowering molecular size of the graft [4].

In respect to surfactants, anionic surfactant such as sodium lauryl sulfate (NaLS) increases the graft yield. The graft is promoted in forms of micelles of NaLS, and the sulfate ions from the Gouy-Chapman double layer. The entanglement of these micelles with silk fibres facilitates the formation of charge transfer complex with the initiator. The concentration of the initiator is increased in the vicinity of the fibre which enhances the free radical formation on the silk backbone, resulting in an increased graft yield [4].

2.7 CHARACTERIZATION OF GRAFT COPOLYMER

The characterization techniques applicable to homopolymers and random copolymers are generally applicable to graft copolymers. However, it must be assumed that the products of intended graft copolymerization are mixtures of graft copolymer, unreacted backbone, and homopolymer of the graft. Sometimes careful analysis reveals only mixtures of homopolymers. The first step in the characterization of a graft copolymer is the determination of whether any graft copolymerization has occurred.

Characterization of surface-grafted copolymers on fibres, films, and plastics is difficult since the yield of graft copolymer is usually very small. However, methods such as attenuated total reflectance (ATR), IR or X-RAY will possibly render the detection of grafting reaction [9,25].

2.8 LITERATURE SURVEY

Graft copolymerization onto fibres, i.e., silk, wool, cellulose, jute, rayon, etc., provides an effective means of improving the fibre properties with minimum degradation of the base polymer. Much interest has been focused on vinyl graft copolymerization of fibres through

chemical initiation by redox systems, because it provides minimum degradation of the base polymer compared with other techniques such as radiation graft copolymerization. Recent works on the study of the graft copolymerization of fibres through initiation by redox systems are listed below.

E. G. Kastning et al. [15] found that metal chelates can be used as initiators in the polymerization of vinyl compounds. Chelates of manganese(III) and Co(III) acetylacetonate are most effective. There is some evidence indicating that the polymerization takes place via a free-radical mechanism. The central metal atom affects the steric configuration of the polymer chain.

C. H. Bamford and D. J. Lind [16] have found that to polymerize methyl methacrylate at 80°C in the presence of a number of acetylacetonates, at concentration of the order of 10^{-3} mole-1^{-1}, manganese(III) acetylacetonate (Mn(acac)$_3$) is an active initiator, Ni(acac)$_2$ V(acac)$_3$ and Cr(acac)$_3$ are weak initiators and that Co(acac)$_3$, TiO(acac)$_2$ and Pb(acac)$_2$ are completely inactive under these conditions.

C. H. Bamford et al. [18] has studied the initiation of vinyl polymerization by manganese(III) acetylacetonate (Mn(acac)$_3$) and manganic 1,1,1-trifluoroacetyl-

acetonate (Mn(facac)₃). In all cases, the polymerization involves a free-radical intermediate. Mn(facac)₃ rapidly initiates polymerization of those monomers which polymerize readily anionically, e.g. methyl methacrylate and acrylonitrile, but Mn(facac)₃ is very much less effective with other monomers such as styrene and vinyl acetate. A mechanism is proposed in which heterolytic fission of an Mn-O bond is followed by addition of the monomer to the anion; the resulting monomer anion then participates in electron transfer with the Mn(III) atom forming Mn(II) and a free radical which is the initiating species.

T. Otsu, N. Minamii, and Y. Nishikawa [18] have reported Mn(acac)₃ to be the best initiator in the homopolymerization of vinyl monomers such as styrene, methyl methacrylate, acrylonitrile, vinyl acetate and vinyl chloride, while Co(acac)₃, Mn(acac)₂, Cu(acac)₂, and Cr(acac)₃ showed moderate activity for the polymerization of MMA at 60°C. The addition of some additives such as halogen compounds did not accelerate the polymerization of MMA by Mn(acac)₃. The initiation mechanism of vinyl polymerization by Me(acac)ₓ was studied on the basis of the complex formation with the monomer.

R. K. Samal et al. [7] has studied the graft copolymerization of methyl methacrylate onto silk fibres

in aqueous solution using Mn(III) acetylacetonate as initiator. The rate of grafting was determined by varying monomer, acidity of medium, temperature and reaction medium. The graft yield increases significantly with an increase of Mn(acac)$_3$ concentration up to 0.01 mole-l^{-1}, but with further increases of Mn(acac)$_3$ the graft yield decreases. The increase in monomer concentration to 0.045 mole-l^{-1} brings about a significant enhancement in the graft yield, and with further increase in the monomer concentration the graft yield decreases. The rate of reaction is temperature dependent; with increasing temperature up to 50°C, the graft yield increases, and with further increase in temperature the graft yield decreases. Among the solvent composition studied, a water/solvent mixture containing 10% of the solvent seems to constitute the most favourable medium for grafting; with further increase in solvent composition, the graft yield decreases.

S. Paulrajan et al.[5] have reported their finding on the kinetics of polymerization of a non-conjugated divinyl monomer, N,N'-methylenebisacrylamide, with a Ce^{IV}-thiourea redox initiating system through cyclopolymerization mechanism which yielded soluble, gel-free polymers.

S. Samal and G. Sahu [21] have studied the graft copolymerization of methyl methacrylate onto mulberry silk

fibres in aqueous solution using Mn(acac)$_3$ as initiator. Perchloric acid was found to catalyze the reaction. The rate of grafting was investigated by varying the concentration of the monomer and the complex, acidity of the medium, the solvent composition of the reaction medium, the surfactant and the inhibitors. The graft yield increases with increasing concentration of Mn(acac)$_3$ up to 0.01 mole-l^{-1}, decreasing thereafter. Increases of MMA concentration up to 0.56 mole-l^{-1} increase graft yield and thereafter it decreases. Among the various monomers studied (i.e., MMA, MA, EA, AN and AA), MMA was found to be most suitable for grafting. Grafting increases up to 7.5 x 10^{-3} mole-l^{-1} of HClO$_4$ concentration, and thereafter it decreases.

K. C. Gupta and S. K. Gupta [4] have investigated the graft of N,N'-methylenebisacrylamide (N,N'-MBA) onto mulberry silk fibres using vanadyl acetylacetonate (VO(acac)$_2$) complex under inert atmosphere at 50°C. The effect of various variables like the concentration of N,N'-MBA and VO(acac)$_2$, the acidity of the medium and the surfactants on the percentage grafting have been investigated. The graft yield increased up to 7.5 x10^{-3} mole-l^{-1} of VO(acac)$_2$ concentration but thereafter it decreased. The higher rate of radical formation has been explained as being due to the coordination of π-electron of the N,N'-MBA with the metal chelate which has assisted in

the cleavage of M-O bond to generate the radical easily. An increase of N,N'-MBA concentration up to 10.0×10^{-3} mole-l^{-1} increases graft yield, and thereafter it decreases. A plausible mechanism for graft copolymerization involving cyclization of N,N'-MBA prior to the grafting has been proposed.

K. C. Gupta, G. D. Raja and K. Behari [25] studied the kinetics of gel-free polymerization of N,N'-MBA by persulfate/ascorbic acid in aqueous medium. The rate of polymerization and percentage conversion was determined. The higher rate of polymerization compared to that of acrylamide was ascribed to an intra-intermolecular mechanism. At low monomer concentration, the propagation occurs by intra-intermolecular linear propagation, but gel is formed at higher concentrations due to the active participation of N,N'-MBA molecules in crosslinking of growing chains, and the chances of linear propagation through the chain cyclization process are reduced.

M. Tsukada [3] has investigated the structural characteristics of 2-hydroxy ethylmethacrylate (HEMA)/ methacrylamide (MAA) grafted silk fibres in various comonomer compositions. Their structural characteristics were studied by X-ray diffractometry, differential scanning calorimetry, and scanning electron microscope. HEMA/MAA-

grafted silk fibres with a graft yield of about 60% obtained in a HEMA/MAA mixture system containing 20% of HEMA and 80% of MAA on a weight basis showed endothermic peaks at $280^{\circ}C$ and $420^{\circ}C$; these are attributed to the thermal decomposition of the MAA and HEMA polymers, respectively, in addition to the thermal decomposition peak of the silk fibroin fibre which appeared at $323^{\circ}C$. The crystalline structure of the HEMA/MAA-grafted silk fibre remained unchanged regardless of the HEMA/MAA grafting ratio even when the graft yield value reached 120%.

M. Tsukada and H. Shiozaki [26] analyzed the structural and physical properties of methacrylonitrile (MAN)-grafted silk fibres in relation to the weight gain on the basis of the results of tensile properties as well as of thermal analysis and x-ray diffractometry. The polymerization treatment with MAN did not affect significantly the tensile properties, i.e., strength and elongation at break of the original fibres. The thermal decomposition of the silk fibroin shifted to higher temperature when the weight gain exceeded 25%, and a constant value at $328^{\circ}C$ was obtained above a weight gain of 40%. The crystalline structure of the silk fibre remained essentially unchanged regardless of MAN treatment.