PART II: GRAFTING ONTO WOOL
INTRODUCTION

Wool is a complex polypeptide, made up of about twenty alpha amino acids. The acids glycine, leucine and isoleucine, proline, cystine and arginine, glutamic acid and aspartic acid make up about two third of its weight. About half of Wool's mass is the main polymer chain and half in the side chains. Since some 30% of the side chains have acid or amine groups along their length, wool is a huge polymeric "Zwitter ion" whose properties and solubility depend markedly upon pH.

Structure:

Wool can exist in both the alpha and beta keratin structures characteristic of the polypeptides with helical and extended sheet structures respectively. The high reversible extensibility of wool (about 30% compared to 5% for cotton) derives from the fact that it can exist in either of these structures.

Microscopic Appearance:

The microscopic appearance of wool is easily recognized by the presence of scales in the epidermal or surface layer of the fiber. These scales give wool the ability to felt or pack into dense stable mats.

Properties of Wool:

Wool is noted for its high moisture absorption (upto 10-15%) and good insulating properties, its wrinkle...
resistance and elastic recovery and its crimpness. Its soil resistance, dyeability and resistance to organic (dry cleaning) solvents are good. On the other hand, it is attacked by moths and mildew, mild alkalis and easily bleaches. It causes allergies. Its strength and stiffness are low compared to those of cotton. It has poor temperature resistance and weatherability in sun light and is adversely affected by hot water, that causes shrinkage and loss of luster and strength.

Despite these drawbacks, the virtues of wool are so great that it probably will continue to find extensive use, as it has to date in suitings and other wearing apparel, blankets, yarns, carpets, felts and upholstery. So far no artificial fiber has equalled it in resilience, hand, insulating properties, dyeability and flame resistance.

Wool is crosslinked through cystine links

\[
\begin{align*}
\text{NHCHCO} & \\
\text{CH}_2 & \\
\text{S} & \\
\text{S} & \\
\text{CH}_2 & \\
\text{OC} & \text{CH} \text{ NH}
\end{align*}
\]

This structure permits swelling but does not impart solubility in organic solvents.
Occurrence

Various sources from which wool is obtained are listed in table I.

Table I
Sources of animal Fibers (Hairs)

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Animal</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wool</td>
<td>Sheep</td>
<td>Widely spread</td>
</tr>
<tr>
<td>Mohair</td>
<td>Angovia goat</td>
<td>Asia minor, S. Africa USA.</td>
</tr>
<tr>
<td>Cashmere wool</td>
<td>Cashmere goat</td>
<td>China</td>
</tr>
<tr>
<td>Camel hair</td>
<td>Bactrian camel</td>
<td>Mangolia, China</td>
</tr>
<tr>
<td>Alpaca</td>
<td>Llama glama Paras</td>
<td>Peru</td>
</tr>
<tr>
<td>Vicuha</td>
<td>Llama Vicuma</td>
<td>Peru</td>
</tr>
</tbody>
</table>

Wool from sheep contains wax, perspiration (suint) dirt and burrs and hence prior to use, wool must be scoured and bleached.

Wool fibers differ in length as well as in mechanical properties and crimp. Some indication of wool characteristics are given in table II.
Table II

<table>
<thead>
<tr>
<th>Type</th>
<th>Breed</th>
<th>Average length</th>
<th>Average diameter (μ)</th>
<th>Counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine</td>
<td>Mirino</td>
<td>1.5-4</td>
<td>10.30</td>
<td>58-90</td>
</tr>
<tr>
<td>Medium</td>
<td>Cheviol</td>
<td>2-4</td>
<td>20-40</td>
<td>46-60</td>
</tr>
<tr>
<td>Medium</td>
<td>Suffolkete</td>
<td>2-4</td>
<td>20-40</td>
<td>46-60</td>
</tr>
<tr>
<td>Long</td>
<td>Cotswold</td>
<td>2-4</td>
<td>20-40</td>
<td>46-60</td>
</tr>
<tr>
<td>Long</td>
<td>Leicester</td>
<td>2-4</td>
<td>20-40</td>
<td>46-60</td>
</tr>
<tr>
<td>Crossbred</td>
<td>Corriedale</td>
<td>2-4</td>
<td>20-40</td>
<td>46-60</td>
</tr>
</tbody>
</table>

In accordance with peptide theory, Hofmeister and Fischer\(^1,2\) found that alpha amino acids are linked through condensation of the carboxyl group of the acid with alpha amino group of another amino acid to form peptide bond. The macromolecule so formed can be represented by the following formula:

\[
H \quad (\text{NH} = \text{CH} - \text{O})_n \text{OH}
\]

(1)

Wool protein contains a large number of functional groups in the side chain and it is logical to assume that many of the chemical reactions of wool protein should be the same as shown by functional groups in simple organic molecules. Various reactions of these functional groups are discussed as follows:
Reactions of various Functional groups present in the side chain of wool proteins

(1) **Reaction of Amino group:**

The amino group will undergo acetylation or reaction with nitrous acid.

\[
\text{--CH}_2\text{NH}_2 + (\text{CH}_3\text{CO}_2)_2\text{O} \rightarrow \text{--CH}_2\text{NHCOCH}_3 \quad \ldots \quad (\text{x})
\]

\[
\text{--CH}_2\text{NH}_2 + \text{HNO}_2 \rightarrow \text{--CH}_2\text{OH} + \text{N}_2 \quad \ldots \quad (\text{y})
\]

The reaction (y) has been used for preparing deaminated wool.

(ii) **Reaction of Threonine and Serine Residues:**

The presence of a pendant hydroxyl group in these acids is responsible for various reactions. When wool is treated with acids (eg. H_2SO_4) used in carbonising process, the hydroxyl group undergoes N-0 peptidyl shift. An interchange between the amide and hydroxyl group of serine or threonine in proteins gives rise to ester.

\[
\text{CH} - \text{CH}_2\text{OH} \quad \text{H}^+ \quad \text{CH} - \text{CH}_2
\]

\[
\text{NH} \quad \text{OH}^- \quad \text{NH}_3 \quad \text{CO}
\]

threonine in proteins gives rise to ester.
(iii) **Reaction of Carboxyl groups:**

The carboxyl groups in wool as provided by the side chains of aspartic and glutamic acid, can undergo esterification with usual reagents as well as with many others eg. alkyl halides, dimethyl sulphate etc. Ethylene oxide is capable of reacting with carboxyl, amino or hydroxyl groups in water soluble proteins.

(iv) **Reaction of Tyrosine Residues:**

Although the presence of tyrosine in wool is very small yet it undergoes various types of reactions due to the presence of p-phenol group in it.

Reaction of wool with iodine gives rise to mono and diiodo derivatives of tyrosine\(^3\).

(v) **Reaction of sulfur containing amino acids:**

In these reactions, both \(-\text{SH}\) and \(-\text{SS}\)- groups in wool appear to play significant role. The disulphide group is very reactive chemically and disruption occurs in most reaction. Various reaction due to disulphide linkages are discussed as follows:

(va) **Reduction:**

Reduction of disulphide linkages gives rise to thiol groups. In case of reaction with thioglycolic acid (TGA), the cleavage of disulphide linkage takes place as follows:
Details of reduction of wool with NaHSO₃ will be discussed in chapter 6 where a complete study on grafting of vinyl monomers onto reduced wool has been described.

Various other reactions that cystine can undergo are listed below:

(Vb) Oxidation
(Vc) Action of light
(Vd) Halogenation
(Ve) Reaction with various chloronating agents
(Vf) Reaction with KCN.

Wool is a fibrous protein and finds extensive applications in industry. The soluble proteins on the other hand are susceptible to denaturation and undergo changes in properties during chemical treatment. Wool, however being a fibrous protein is stable and can be subjected to chemical treatment without damaging its textile properties. Thus modification of wool can be effected by grafting appropriate vinyl monomers in presence of a variety of initiating systems.

Methods of Modification of Wool:

Two methods are primarily used for effecting modification of wool. These are:
1. **Formation of cross-linkages:**

Cross linkages impart important contributions to the properties of wool; and these are: greater resistance in most solvents, limited lateral swelling and relatively high wet strength. Various methods that can be readily employed for the introduction of cross linkages in wool are discussed as follows:

1(i) **Polyfunctional Alkylating Agents**

Reaction of chloro methyl ethers (I) with wool when applied from organic solvents, will give rise to a product having increased tensile strength, reduced alkali solubility, and decreased tendency towards supra contraction. Following reaction takes place:

\[
\text{RNH}_2 + \text{ClCH}_2\text{OCH}_2\text{Cl} \rightarrow \text{RNHCH}_2\text{OCH}_2\text{Cl}
\]  
(I)

\[
\text{RNH} - \text{CH}_2\text{O} - \text{CH}_2\text{Cl} + \text{RCOOH} \rightarrow \text{RNHCH}_2\text{OCH}_2\text{OCR}
\]

Other bifunctional reagents that have been tried are ethylene imines, 1,3-difluoro, and 4,6-dinitrobenzene bisepoxide.

1(ii) **Reagents that can rebuild reduced disulfide bonds**:

Alkyl bromide (II) can form a cross linkage with thiol group obtained by reduction of disulfide bond.
Modified wool so obtained was found to be more resistant towards reagents such as alkali, acids, oxidizing and reducing agents.

1(iii) Reaction with Formaldehyde:

If wool is steeped in formaldehyde solution, methylol groups are formed with the amino acid lysine present in wool.

\[ \text{RNH}_2 + \text{HCHO} \rightarrow \text{RNHCH}_2\text{OH} \]

Lysine thus becomes less basic.

Reaction of methylol groups with the acid amide groups of glutamine produces stable linkages as follows:

\[ \text{RNHCH}_2\text{OH} + \text{H}_2\text{NCOR} \rightarrow \text{RNHCH}_2\text{NHCOR} \]

2. Graft copolymerization:

In recent years, chemical modification of wool through grafting has received considerable interest.\(^{(7-9)}\) Grafting promises to be a powerful tool for producing considerable modification of wool properties. During grafting care must be taken for proper initiation so that the radicals are formed on the fibers, which will initiate polymerization of monomer
diffusing into the interior of the wool.

The exact location of polymers in the wool fiber is important with regard to the properties of modified wool. Polymers grafted onto surface of wool tend to alter fiber assemblies made from wool, but without any effect on single fiber properties.

Various methods have been used for the deposition of polymers on wool fibers. Important ones are

2(i) Spontaneous initiation in presence of swelling agents.
2(ii) Radiation induced grafting.
2(iii) Chemical initiation.

2(i) **Spontaneous initiation**:

Williams and Stannett\(^{(10)}\) investigated the method of spontaneous initiation for grafting in the presence of swelling agents. Wool in contact with an aqueous solution of ethyl acrylate is spontaneously grafted at rapid rates. The initiation of grafting occurs through free radical formation and is thought to be caused by solvent penetration.

2(ii) **Radiation induced grafting**:

The radiation induced grafting of various vinyl monomers to a wide variety of natural and synthetic substrates has been investigated extensively\(^{(11)}\). However little attention has been paid to radiation induced grafting to wool fibers.
Radiation grafting may be initiated by two techniques, e.g., preirradiation technique and mutual irradiation technique. Usually mutual method leads to much larger amounts of polymer being grafted to wool.

2(iii) Chemical Initiation:

Various methods of chemical initiation yield free radicals which are not necessarily part of the substrate and the covalent bond may be formed between the substrate and added polymer by chain transfer. Methods of chemical initiation include:

(a) Ceric ion initiation (f) Copper(II) complex trichloro acetic acid initiation.
(b) Periodate initiation (g) Redox systems.
(c) Peroxydisulphate initiation (h) DMA - Benzyl chloride
(d) Manganese ion initiation (i) Dye sensitized photo initiation.
(e) Initiation by radical initiations. (j) Miscellaneous.

(a) Ceric ion initiation:

Ce(IV) has been widely used as an initiator for vinyl\textsuperscript{(12-14)} polymerization and grafting. By this method grafting efficiency has been observed to be much higher than any other method\textsuperscript{(15)}. Kantouch, Hebeish and Bendak\textsuperscript{(16, 26)} used Ce(IV) for initiation of grafting of MMA onto wool. With exception of KCN-treated wool, grafting was accompanied by the formation of large amount of homopolymer. Following mechanism has been suggested for Ce(IV) ion initiated grafting onto wool.
Initiation

\[ WH + Ce^{4+} \xrightarrow{K} W^- + H^+ + Ce^{3+} \]  

(1)

where \( WH = \) Wool and \( M = \) Monomer

Propagation

\[ WM^- + nM \xrightarrow{k_p} WM_{n+1}^- \]  

(3)

Termination

\[ WM_{n+1}^- + Ce^{4+} \xrightarrow{K_t} WM_{n+1}^- + H^+ + Ce^{3+} \]

\( Ce^{4+} \) may also attack wool radical giving rise to various oxidation products.

\[ W^- + Ce^{4+} \rightarrow \text{Oxidation product of Wool} + H^+ + Ce^{3+} \]

Misra et al\(^{(17,18)}\) carried out grafting of poly(methylacrylate) and poly(ethyl acrylate) onto wool using ceric ammonium nitrate (CAN) as initiator. Addition of nitric acid was found to catalyze the grafting reactions. Reactivities of various monomers towards grafting onto wool in presence of CAN have been determined\(^{(19)}\). Following order of reactivity was observed \( MA > EA > MMA > VAc > AAC \).
Recently Misra et al. (20) studied the effect of various amines upon ceric ion initiated grafting of poly(methyl methacrylate) onto wool. An explanation based on the basicity, nucleophilicity and steric requirement of amine was given to explain the following reactivity order shown by various amines towards graft copolymerization. \( \text{DEA} \rightarrow \text{DPA} \rightarrow \text{NH}_3 \rightarrow \text{TEA} \rightarrow \text{Triethanol amine} \rightarrow \text{Py} \).

(b) **Periodate initiation**

Using sodium periodate as initiator Kantouch, Hebeish and Bandak (21) carried out successfully the grafting of MMA onto wool. Both oxidation of wool and polymerization were found to occur simultaneously.

(c) **Peroxy disulphate initiation**

Various workers have used peroxy disulphate initiation for effecting grafting of various vinyl monomers onto wool (22-25). A detailed study of peroxy disulphate initiation for grafting onto wool and reduced wool has been discussed in chapters 5 and 6.

(d) **Manganese ion initiation**

Only a few studies have been reported on the use of manganese ion as initiator for grafting onto textile fiber (26,27). Hebeish et al. (27) have studied the \( \text{Mn}^{2+} \)-initiated grafting of MMA onto wool. Temperature was found to have a pronounced effect on the graft yield.
(e) **Initiation by Radical Initiators:**

Both BPO and AIBN are widely used as initiators for vinyl polymerization. AIBN in presence of different solvents has been used by Bendak and Hebeish for effecting grafting of MMA onto wool fibers. Effect of Ce as additive in AIBN initiated grafting of MMA onto wool has been studied by Kontouch et al. A considerable increase in percent grafting was observed. Similar behavior was also observed in case of BPO which alone was found incapable of effecting grafting onto wool.

Recently Misra and Chandel have used BPO in presence of an acetic acid-Pyridine mixture which acts as pH modifier for grafting polystyrene onto wool fibers. It was observed that acetic acid-Pyridine mixture acts both as a pH modifier and swelling agent.

(f) **Copper(II) complex Trichloroacetic Acid Initiation:**

Copper(II) acetyl acetonate and trichloroacetic acid has been used to initiate polymerization of various acrylate monomers inside wool fibers. Production of free radicals on the wool backbone has been possible by a complex formed between trichloro acetic acid or its ammonium salt and bis(acetylyacetone) - copper(II) complex. No homopolymer was observed during grafting.
(g) **Redox systems**: *(Fenton's Reagent)*

Since the work of Lipson and Speakman\(^{(34)}\), this reagent has been successfully used for grafting of various vinyl monomers onto wool.\(^{(35)}\) Polymerization inside the wool fibers is initiated by the OH formed by the reaction of Fe\(^{+2}\) with H\(_2\)O\(_2\).

\[
\begin{align*}
\text{Fe}^{+2} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{+3} + \text{OH} + \text{OH}^-
\text{OH} + \text{Fe}^{+2} & \rightarrow \text{OH}^{-} + \text{Fe}^{+3}
\text{OH} + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O} + \text{HO}_2^-
\text{HO}_2^- + \text{H}_2\text{O}_2 & \rightarrow \text{OH} + \text{H}_2\text{O} + \text{O}_2
\end{align*}
\]

This system has been used for depositing within the wool fibers of polymers and copolymers from a number of vinyl monomers\(^{(36)}\). Recently Misra et al\(^{(37)}\) have successfully graft copolymerized Poly(VAc) onto wool using Fenton's reagent as redox initiator. It was found that molar ratio of \(\frac{[\text{FAS}]}{[\text{H}_2\text{O}_2]}\) has a pronounced effect on percent grafting. Maximum grafting was observed at the molar ratio of \(\frac{[\text{FAS}]}{[\text{H}_2\text{O}_2]} = 1.43:1\).

(h) **DMA - Benzyl Chloride initiator**

Bendak et al\(^{(47)}\) have used DMA - Benzyl chloride mixture as initiator for effecting grafting of MMA onto wool. The nature of the solvent was found to influence both grafting and homopolymerization. EtOH was found to be the best solvent.
(i) **Dye Sensitized Photo Initiation:**

Dye sensitized photo polymerization of acrylic monomers is well studied\(^{[48-51]}\) and recently some workers have also been able to deposit polymer within wool by this method\(^{[52-54]}\). Horio et al\(^{[55]}\) have reported riboflavin sensitized photo-polymerization of acrylamide in presence of wool. -SH group present in wool was found to play an important role during grafting.

Grafting of acrylic monomers to wool sensitized by anthraquinone has been carried out by Needle et al\(^{[54]}\). Formation of lesser amount of homopolymer with lower molecular weight was observed.

(ii) **Miscellaneous systems:**

Malcomet et al\(^{[56]}\) have reported grafting of vinyl monomers onto wool by the action of electric charges and UV radiation. Internal disposition within wool has also been initiated by BPO\(^{[8]}\). Kojima et al\(^{[57]}\) have used Bu\(_3\)B-water system for grafting of MMA onto wool. Grafting of vinyl monomers onto wool has been achieved by diazotization\(^{[58]}\). Grafting by this method eliminates some steps which degrade wool fiber.
CHAPTER 5

GRAFTING OF VINYL MONOMERS ONTO WOOL BY USING POTASSIUM PERSULPHATE - FERROUS AMMONIUM SULPHATE (KPS-FAS) SYSTEM AS REDOX INITIATOR
INTRODUCTION

This chapter describes the detailed chemistry involved in the grafting of vinyl acetate (VAc) and methyl acrylate (MA) onto wool, by using potassium persulfate - ferrous ammonium sulphate (KPS-FAS) system as the redox initiator.

The role of sulphur compounds in modifying, initiating or promoting polymerization has been recognized for many years. It is therefore natural that efforts would be made to attempt grafting onto wool by using a redox system, one component of which is a sulphur containing compound. Grafting onto wool protein, through reactions involving sulfur has been extensively studied.

Persulfate such as Ammonium persulphate (APS), Sodium persulphate (NaPS) and Potassium persulphate (KPS) are excellent polymerization initiator in aqueous medium. In analogy with H₂O₂ decomposition, their activity could be attributed to sulphate radical anions, formed by the homolytic fission:

\[-\text{OSO}_2\text{O}^-\text{OSO}_2\text{O} - \rightarrow 2(\text{OSO}_2\text{O})^-\]

The kinetics of persulphate decomposition in aqueous solution, which in the absence of polymerizable substances, leads to oxygen evolution have been studied by several workers. Oxygen evolution was proved by Kolthoff and Miller (59) who suggested the following mechanism for the decomposition of
persulphate in aqueous medium.

\[ S_{2}O_{8}^{2-} \rightarrow 2SO_{4}^{2-} \]

\[ SO_{4}^{2-} + H_{2}O \rightarrow HSO_{4}^{-} + HO^{-} \]

\[ 2H_{2}O \rightarrow H_{2}O + \frac{1}{2}O_{2} \]

During vinyl polymerization by redox mechanism following steps occur:

\[ M^{+2} + ROOR \rightarrow M^{+} + RO^{-} + OR^{-} \]  \hspace{1cm} (a)

\[ M + RO^{-} \rightarrow ROM^{-} \]  \hspace{1cm} (b)

\[ M \rightarrow RO - (M)_{n} \]  \hspace{1cm} (c)

Termination may occur by (i) recombination (ii) disproportionation and (iii) chain transfer.

\[ RO - (M)_{n}^{+} + RO - (M)_{n}^{+} \rightarrow RO - (M)_{n}^{+} - (M)_{n} - OR \]  \hspace{1cm} (d)

\[ R - (M)_{n}^{+} + HA \rightarrow RO - (M)_{n}^{+}H + A^{-} \]  \hspace{1cm} (e)

'OR may be destroyed by another process.

\[ M^{+2} + 'OR \rightarrow M^{3+} + OR^{-} \]  \hspace{1cm} (f)

'OR may also be destroyed by

\[ HB + 'OR \rightarrow HOR + B^{-} \]  \hspace{1cm} (g)
Steps (a) and (g) are commonly postulated during oxidation of organic compound by redox system.

EB is any readily oxidisable substance which may be present.

Steps (b-d) (OR = SO\textsuperscript{4-}) would result in the incorporation of sulphate end groups in polymers of high molecular weight\textsuperscript{(60)}.

Since the time the mechanism of redox catalysts first came under discussion, the formation of sulphate radical by "one electron transfer" between persulphate and reducing agent has been considered\textsuperscript{(61)}. Electron transfer between persulphate and monomer was also considered as a likely process for initiation.

\[ \text{S}_2\text{O}_8^{2-} + M \rightarrow (\text{SO}_4\text{M}^{n+}) + \text{SO}_4^{2-} \]

But it was pointed out by Kolthoff\textsuperscript{(62)} that no such process is occurring.

Persulphate initiated polymerization is greatly accelerated by compounds which react with persulphate, and these are:

(i) metals
(ii) oxidisable metal salts
(iii) hydrazine
(iv) hydrogen sulphide
(v) RSH
(vi) Salts of oxacids of sulphur, e.g., sulphite, dithionate and thiosulphate
(vii) polyhydric phenols
One of the best investigated of such redox systems is Fe$^{+2}$ - S$_2$O$_8^{2-}$. Kolthoff$^1(63)$ and Williams$^2(64)$ have postulated the following primary step.

$$\text{Fe}^{+2} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{+3} + \text{SO}_4^{2-} + \text{SO}_4^{2-}$$

As with Fe$^{+2}$ - H$_2$O$_2$ system, the Fe$^{+2}$ - S$_2$O$_8^{2-}$ reaction also produces oxygen. Bromide ion (Br$^{-}$) and chloride ion (Cl$^{-}$) suppress oxidation of a substrate by competition for radical ion.

$$\text{SO}_4^{2-} + \text{Br}^{-} \rightarrow \text{SO}_4^{2-} + \text{Br}^{-}$$

$$\text{Fe}^{+2} + \text{Br}^{-} \rightarrow \text{Fe}^{+3} + \text{Br}^{-}$$

According to Merz and Waters$^3(65)$ similarity exists between the action of Fe$^{+2}$ - H$_2$O$_2$ and Fe$^{+2}$ - S$_2$O$_8^{2-}$ towards oxidation of alcohols, so the initiation process in both the cases is of the same type.

$$\text{Fe}^{+2} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{+3} + \text{HO}^{-} + \text{OH}$$

$$\text{Fe}^{+2} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{+3} + \text{SO}_4^{2-} + \text{SO}_4^{2-}$$

Kolthoff differed from this conclusion with respect to the following when alcohol is the substrate.

$$\text{Fe}^{+2} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{+3} + \text{SO}_4^{2-} + \text{SO}_4^{2-}$$

$$\text{CH}_3\text{CH}_2\text{OH} + \text{SO}_4^{2-} \rightarrow \text{CH}_3\text{-CH} - \text{OH} + \text{SO}_4\text{H}^{-}$$

$$\text{CH}_3\text{-CH} - \text{OH} \rightarrow \text{CH}_3 - \text{CH} = 0$$
Persulphate also forms redox system with Ag⁺.

Complex salts of heavy metals as activators in persulphate initiated polymerization:

Ferricyanide\(^{(66)}\) and various cobalt complexes\(^{(67)}\) have been found to act as activator. Little is known about the chemistry of these processes which are complicated by the fact that some multivalent metal ions appear to be able to initiate polymerization without the aid of peroxidic compounds.

Thiols as Activators:

Thiols are best studied of nonmetal activating agents for S\(_2\)O\(_8\)^{2⁻}. These are introduced as `modifiers' long back and their function as regulator of polymer growth through radical transfer step is well known.

\[
\begin{align*}
  x - (\text{CH}_2 - \text{CH} \_x) & \_n + \text{RSH} \rightarrow x (\text{CH}_2\text{CH} \_x) \_n \\
  & \text{R} + \text{RS}.
\end{align*}
\]

Rs (thiyl radical) in turn can initiate further polymerization.

\[
\begin{align*}
  \text{CH}_2 = \text{CH} \_x + \text{RS} \rightarrow \text{RS} \text{CH}_2\text{CH} \_x.
\end{align*}
\]

Kolthoff\(^{(68)}\) has shown that thiols not only modify the properties of the polymers but also increase polymerization speed. From kinetic studies, Eager and Winkler\(^{(69)}\) suggested the following scheme to describe activating effect of thiols.
A typical system that uses thiols is

\[ \text{M - Soap} \rightarrow \text{S}_2\text{O}_8^{2-} \rightarrow \text{RSH} \]

\[ \text{S}_2\text{O}_8^{2-} - \text{HSO}_3^- \text{ system :} \]

The activating effect is to enhance polymerization by the addition of small amounts of heavy metals ions such as iron, silver etc. From a study of ethylene polymerization, it was concluded that radical producing reaction in \( \text{S}_2\text{O}_3^{2-} - \text{HSO}_3^- \) system are the following \( \text{(70)} \):

\[ \text{Fe}^{+2} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{+2} + \text{SO}_4^{2-} + \text{SO}_4^- \]

\[ \text{Fe}^{+3} + \text{HSO}_3^- \rightarrow \text{Fe}^{+2} + \text{HSO}_3^- \]

\[ \text{S}_2\text{O}_8^{2-} + \text{HSO}_3^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^- + \text{HSO}_3^- \]

\[ \text{S}_2\text{O}_8^{2-} - \text{S}_2\text{O}_3^{2-} \text{ system :} \]

Morgan \( \text{(71)} \) observed that activity of \( \text{S}_2\text{O}_8^{2-} - \text{S}_2\text{O}_3^{2-} \) system is greatly enhanced by addition of small amounts of \( \text{Cu}^{2+}, \text{Fe}^{2+} \) \text{ or I}^- \text{ ions}. Bunn advanced a tentative mechanism with the primary step.

\[ \text{S}_2\text{O}_8^{2-} + \text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-} + \text{SO}_4^- + \text{S}_2\text{O}_3^- \]
The use of persulphate in initiating graft polymerization in proteins was illustrated by Madras and Speakman(19) who found that when wool is treated with persulphate and methacrylic acid at 25°C for 1 hour, large amounts of polymer is formed, the weight increase in wool being as high as 49%. With persulphates as initiator, acrylonitrile can be polymerized in wool fibers in a short time(20). Persulphate however alters the mechano-chemical properties of wool to a much greater extent than H₂O₂ - ferrous ion initiator system, which has little or no effect on these properties. The following initiation mechanism was suggested by Speakman and coworkers for grafting of vinyl monomers onto wool in presence of persulfate.

\[ R - S - S - R \rightarrow 2 R - S^\cdot \]
\[ R - S^\cdot + S_2O_8^- \rightarrow R - S - O - SO_3^- + SO_4^- \]
\[ R - S - O - SO_3^- \rightarrow RS^\cdot + SO_4^- \]
\[ SO_4^- + H_2O \rightarrow HSO_4^- + \cdot OH \]

Aral et al (72) were successful in preparing graft copolymers of Poly(MMA) and wool by using aqueous K₂S₂O₈(72,73) and dimethyl sulfoxide - K₂S₂O₈(73). From the end group data, they presented evidence that all the internally deposited polymer was truly grafted on the wool chains and all reactions in deactivation of the polymer radicals were probably due to termination between the two growing radicals.
Arai et al.\(^{(74)}\) also reported that when a small amount of persulphate is dissolved in a relatively concentrated aqueous solution of bromide salts, especially LiBr, liberation of \(\text{Br}_2\) occurs to some extent and this system can be successfully utilized for the grafting of various acrylates in wool fiber. This new graft copolymerization has been attributed to the concerted action of the fiber swelling power of bromide salts, the following redox system and the mild bromination of some monomers by which grafting will proceed without homopolymerization.

\[
\text{Br}^- + S_2O_8^{2-} \rightarrow \text{Br}^+ + S_0^7^- + S_0^{4-}
\]

\[
\text{Br}^+ + \text{Br}^- \rightarrow \text{Br}_2
\]

No homopolymer was obtained\(^{(75)}\) during grafting of MMA onto wool fibers, using aqueous LiBr - \(K_2S_2O_8\) as initiation system. It was observed that at a given concentration of redox catalysts (LiBr - \(K_2S_2O_8\)), the thiol groups in wool fibers provided sites for grafting. The nature of termination reaction in the polymerization of MMA and styrene in a viscous matrix of wool fibers was studied\(^{(74)}\) and it was noted that at a constant disulfide content in the fibers, the thiol anion becomes the determining factor for the termination.

Lohani and coworkers\(^{(23)}\) used \(S_2O_8^{2-}\) in presence of \(H_2SO_4\) as initiating system for deposition of 20-25\% of Poly(AN) on wool. Wolfram and Menkart\(^{(24)}\) and other workers\(^{(25)}\) have used
persulphate initiation in presence of oxygen scavenger such as tetra bis hydroxy methyl phosphonium chloride (THPC) for polymerization of acrylic monomer inside the wool. This method is the most successful one for commercial deposition of polymers onto wool.
EXPERIMENTAL

Materials and Method

(a) Purification and Physical Characterization of Wool:

Himachali wool was purified by extraction with a mixture of acetone and petroleum ether in the soxhlet apparatus for 48 hours. The wool was then washed with water and dried at 50°C.

The physical characterization of wool was carried out with respect to the following:

(i) Moisture content:

One gram of wool was placed in an oven maintained at 110°C for one hour. The loss in weight gives the moisture content in the wool.

(ii) Acetone Soluble Fraction

Weighed amount of wool was extracted with acetone in soxhlet apparatus for 48 hours. After extraction wool was dried at 50°C and weighed to the constant weight. The loss in weight was noted.

(iii) Ash Content:

One gram of wool was placed in a silica crucible, which was placed in the furnace at 1000°C until complete combustion occurred. The loss in weight is calculated. Results are reported in table V.
(b) **Purification of Monomers:**

Methyl acrylate (MA) (BDH) and vinyl acetate (VAc) (BDH) were purified by the methods described in chapter 1.

(c) **Purification of Nitrogen:**

Nitrogen was purified by the same method as described in chapter 1.

Potassium persulfate (KPS) (BDH) was used as received and Ferrous ammonium sulfate (FAS) (BDH) was recrystallized from water before use.

**Graft Copolymerization**

Pure Himachali wool (1.0 gm) was dispersed in 300 ml of cold deaerated distilled water, in a three-necked flask. The wool dispersion was purged with purified nitrogen under constant stirring for thirty minutes and the temperature of the wool dispersion was brought to the water bath temperature. A definite amount of KPS and FAS was added to the reaction flask. The flask was again purged with nitrogen for another thirty minutes, and then a continuous supply of nitrogen was maintained throughout the reaction periods. Known amount of monomer (VAc or MA) was added dropwise to the reaction mixture. The copolymerization reactions were carried out at different temperatures for different reaction periods.
After completion of the reaction, the reaction mixture was filtered and the residue was extracted for 48 hours with benzene for the removal of homopolymer Poly(VAc) or Poly(MA).

After complete removal of homopolymer, the residue so obtained was dried at 50°C in the oven until constant weight is obtained. Percentage grafting and percent efficiency were determined from the increase in the initial weight of the wool by the following method.

\[
\text{Percent grafting} = \frac{W_1 - W_0}{W_0} \times 100
\]

\[
\text{Percent Efficiency} = \frac{W_1 - W_0}{W_2} \times 100
\]

where \(W_0\), \(W_1\) and \(W_2\) denote respectively the weights of wool, grafted wool after benzene extraction and the weight of the monomer added.

The results are presented in tables I and II. Initial rates of reaction were determined from the slopes of percentage of grafting versus time (Figs. No. 1 and 2). Rate of grafting (\(R_p\)) and induction period (\(I_p\)) as determined from the plots are presented in tables III and IV.

Evidence of grafting:

(1) A physical mixture of Poly(VAc) or Poly(MA) and wool were prepared by dispersing wool in benzene solution of Poly(VAc) or Poly(MA). This dispersion was stirred for 24 hours and filtered. The residue so obtained was extracted with benzene.
for 48 hours. After extraction, the residue was hydrolyzed with 6NHCl at 115°C for 24 hours. No residue of Poly(VAc) or Poly(MA) was obtained, indicating thereby that benzene extraction completely removes homopolymer.

(ii) Wool-g-Poly(MA) was refluxed with 6NHCl at 115°C for 24 hours. The resinous mass obtained after refluxing was identified as Poly(MA). Grafted Poly(VAc) could not be isolated from the hydrolysis of wool-g-Poly(VAc) since during hydrolysis some Poly(VAc) was converted into Poly(vinyl alcohol) which is soluble in water. The isolation of Poly(MA) from the grafted material after HCl treatment, constituted evidence of grafting.

(iii) The infrared spectrum of wool-g-Poly(VAc) and wool-g-Poly(MA) showed absorption at 1720 cm⁻¹ and 1730 cm⁻¹ respectively, attributed to C=O of Poly(VAc) and Poly(MA) (Figs. 3 and 4). No such band was observed in the spectrum of wool (Fig. 5).

(iv) Changes in the solubility of wool fiber following grafting may also provide indirect evidence of grafting. Following four media were used, for carrying out the solubility tests of wool and grafted wool.

(a) Urea bisulfite treatment:

Wool was treated with a solution of 3% sodium meta bisulfite and 50% urea for one hour at 65°C. pH was maintained at 7.0 and the loss in weight was recorded.
The same treatments were also given to the grafted wool and the loss in weight was recorded in every case.

(b) **Alkali treatment**: Wool was treated for 1 hour with 0.1N NaOH at 65°C and the loss in weight was measured.

(c) **Acid Treatment**: Wool was treated with 4M HCl for one hour at 65°C and the loss in weight was recorded.

(d) **Oxidizing Solvents**: Wool was dispersed in 2% per acetic acid for 25 hours at room temperature and then treated with 0.3% aq. ammonia. Loss in weight was recorded. The results are presented in table VI.

(v) **Comparison of scanning electron micrograph of wool** (Fig.6) and wool-g-Poly(MA) (Fig.7) showed that considerable amount of Poly(MA) was deposited onto the wool surface.
RESULTS AND DISCUSSION

KPS is known to enter into redox reaction with Fe$^{+2}$. In analogy with the reaction of Fe$^{+2}$ with $\text{H}_2\text{O}_2$, the following reaction can be written for interaction of Fe$^{+2}$ with persulphate.

$$\text{Fe}^{+2} + \text{SO}_4^{2-} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} \quad \text{(1)}$$

In presence of aqueous medium, $\text{SO}_4^{2-}$ can further interact with water to generate $\cdot\text{OH}$ which is responsible for initiation of vinyl polymerization and graft copolymerization. The following mechanism is suggested for grafting of poly(VAc) and Poly(MA) onto wool in presence of KPS-FAS system.

$$\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \cdot\text{OH} \quad \text{(2)}$$

$$\text{W} + \cdot\text{OH} \rightarrow \text{W}^+ + \text{H}_2\text{O} \quad \text{(3)}$$

$$\text{M} + \cdot\text{OH} \rightarrow \text{OH} - \text{M}^+ \rightarrow \text{OH} - \text{M}^+ \quad \text{(4)}$$

$$\text{OH} - (\text{M})_{n+1} + \text{W} \rightarrow \text{OH} - (\text{M})_{n+1} - \text{H} + \text{W}^+ \quad \text{(5)}$$

$$\text{W}^+ + \text{M} \rightarrow \text{WM}^+ \rightarrow \text{W} - (\text{M})_{n+1} \quad \text{(6)}$$

$$\text{W} - (\text{M})_{n+1} + \cdot\text{OH}(\text{M})_{n+1} \rightarrow \text{W} - (\text{M})_{2n+2} + \text{OH} \quad \text{(7)}$$

$$\text{W} - (\text{M})_{n+1} + \text{Fe}^{3+} \rightarrow \text{W} - (\text{M})_{n+1} + \text{Fe}^{+2} \quad \text{(8)}$$
It is apparent from the above postulated mechanism (eq.1-8) that both SO₄²⁻ and OH may be involved in grafting reaction. However, since the concentration of persulphate is very small, initiation of grafting by SO₄²⁻ seems unlikely, when grafting is carried out in the absence of swelling agents. Penetration by SO₄²⁻ can occur within the fiber only when fiber is preswelled by appropriate swelling agent. In the present study, no such swelling agent was used. Further, in aqueous medium, SO₄²⁻ immediately reacts with water to generate OH. Once the formation of OH is rationalized, it is easier to explain grafting by the same mechanism as proposed for grafting of vinyl monomers in presence of Fenton's reagent. The OH radical can easily abstract hydrogen atom from wool backbone (W) to generate the macro radical (W) which can interact with vinyl monomer to produce graft. Further, OH can initiate vinyl polymerization and the resulting growing polymeric chain can also generate macro radical (W) by hydrogen abstraction. Termination of the growing grafted chain can occur by either process (7) or (8) or by both. Since Fe⁺³ is involved in termination of the growing grafted chain, its presence will have profound effect on graft yield.

This indicates that relative amount of KPS and FAS should influence grafting.

Tables I and II show that maximum graft yield occurs when the molar ratio of \[
\frac{[\text{FAS}]}{[\text{KPS}]} = 0.713 : 1
\] When the ratio
of \( \frac{[\text{FAS}]}{[\text{KPS}]} \) exceeds the optimum value, percent grafting decreases considerably. This indicates that a higher \( \frac{[\text{FAS}]}{[\text{KPS}]} \) value, more of \( \text{Fe}^{3+} \) is formed by interaction with KPS which participates in termination of growing grafted chain. When the molar ratio of \( \frac{[\text{FAS}]}{[\text{KPS}]} \) is less than optimum value, then also percent grafting decreases. This may indicate that at lower \( [\text{Fe}^{2+}] \) concentration of \( \cdot \text{OH} \) is very less. Thus, it is observed that during grafting by KPS-FAS system, there exists a critical concentration of KPS and FAS at which grafting is maximum. Similar behaviour of the molar ratio \( \frac{[\text{Fe}^{2+}]}{[\text{H}_2\text{O}_2]} \) was observed during grafting of Poly(VAc) onto wool\(^{(19)}\) in presence of Fenton's reagent. Maximum percent grafting of VAc \(^{(19)}\) occurred at the molar ratio of \( \frac{[\text{Fe}^{2+}]}{[\text{H}_2\text{O}_2]} = 1:43:1. \) Percent grafting decreased when the molar ratio of \( \frac{[\text{Fe}^{2+}]}{[\text{H}_2\text{O}_2]} \) was higher or lower than the critical value.

In accordance with the mechanism suggested above, increase in the concentration of vinyl monomer should enhance grafting. It is observed from tables I and II that with increase in monomer concentration, percent grafting increases with both MA and VAc and reaches maximum value (92.5%) at a MA concentration of 0.11 mole/litre and (32.5%) at VAc concentration of 0.36 mole/litre.

At higher monomer concentration, percent grafting decreases with both VAc and MA. This is explained by the fact that at higher monomer concentration, homopolymerization assumes importance. It is important to note that MA affords maximum grafting at a much
lower concentration than VAc. This may reflect upon the relative reactivities of these two types of monomer towards free radical reactions. Less grafting obtained with VAc is explained by the fact that VAc being susceptible to hydrogen transfer reaction is wasted in side reactions in the following manner.

\[
\begin{align*}
\text{CH}_2 &= \text{CH} - \text{O} - \text{C} - \text{CH}_3 + \cdot \text{OH} \\
\text{CH}_2 &= \text{CH} - \text{O} - \text{C} - \text{CH}_2 \\
\downarrow \\
\text{CH}_2 &= \text{CH} - \text{O} - \text{C} = \text{CH}_2
\end{align*}
\]

No such monomer transfer reactions are possible with MA since upon hydrogen abstraction MA affords a radical species which is not resonance stabilized.

\[
\begin{align*}
\text{CH}_2 &= \text{CH} - \text{O} - \text{CH}_3 + \cdot \text{OH} \\
\text{CH}_2 &= \text{CH} - \text{O} - \text{C} - \text{CH}_2 \\
\downarrow \\
\text{CH}_2 &= \text{CH} - \text{O} - \text{C} = \text{CH}_2
\end{align*}
\]

In order to investigate the effect of temperature several grafting reactions were carried out at different temperatures. It is observed from tables I and II that both VAc and MA afford maximum grafting at 60°C. At higher temperature, considerable homopolymer formation occurred that led to decrease in percent grafting. This will be expected since various hydrogen abstraction reactions are accelerated at higher temperature leading to wastage of vinyl monomer.
Effect of time and determination of rate of grafting (Rp) and induction period (Ip)

Further it can be seen from tables I and II that the percentage of grafting increases with increase in time. Maximum percentage of grafting (92.5%) and (32.5%) was observed in case of MA and VAc within 150 and 120 minutes respectively. Percent grafting of VAc and MA were plotted against time (Figs. 1 and 2). Induction period (Ip) and initial rate of grafting (Rp) were determined from these plots. The values of Ip and Rp as determined from these plots are presented in tables III and IV. The rate of grafting (Rp) as well as induction period (Ip) are affected by total initial monomer concentration. Further, it is observed that methyl acrylate at a concentration of 0.11 mole/litre affords higher grafting rate (Rp = 2.09%/minute) with induction period, Ip = 87 minutes. With increase in monomer concentration, both Rp and Ip decrease. This may indicate that MA at lower concentration favours grafting. In case of VAc, it can be seen from Fig.1 that both Rp and Ip increase with increase in monomer concentration. Maximum values of Rp = 0.47%/minute and Ip = 58.5 minutes were obtained at VAc concentration equal to 36 mole/litre. This tends to indicate that VAc being less reactive towards radicals, affords grafting only at higher concentration.

Thus it may be concluded from the foregoing discussion that vinyl monomers differ in reactivity towards grafting onto wool in presence of KPS-FAS redox initiator and that MA is more reactive than VAc.
Table I

Effect of concentration of monomer (VAC) and molar ratio of [FAS]/[KPS] temperature and time upon FAS - KPS system initiated grafting onto wool.

<table>
<thead>
<tr>
<th>S-No.</th>
<th>Molar ratio of [FAS]/[KPS]</th>
<th>Conc. of monomer in mole/litre</th>
<th>Temp. °C</th>
<th>Time in minutes</th>
<th>% age Grafting</th>
<th>% age Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.713:1</td>
<td>0.18</td>
<td>40</td>
<td>120</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.</td>
<td>0.713:1</td>
<td>0.18</td>
<td>45</td>
<td>120</td>
<td>5.7</td>
<td>1.2</td>
</tr>
<tr>
<td>3.</td>
<td>0.713:1</td>
<td>0.18</td>
<td>50</td>
<td>120</td>
<td>7.7</td>
<td>1.6</td>
</tr>
<tr>
<td>4.</td>
<td>0.713:1</td>
<td>0.18</td>
<td>60</td>
<td>120</td>
<td>12.7</td>
<td>2.7</td>
</tr>
<tr>
<td>5.</td>
<td>0.713:1</td>
<td>0.106</td>
<td>60</td>
<td>120</td>
<td>5.1</td>
<td>1.8</td>
</tr>
<tr>
<td>6.</td>
<td>0.713:1</td>
<td>0.25</td>
<td>60</td>
<td>120</td>
<td>18.4</td>
<td>2.6</td>
</tr>
<tr>
<td>7.</td>
<td>0.713:1</td>
<td>0.36</td>
<td>60</td>
<td>120</td>
<td>32.5</td>
<td>3.3</td>
</tr>
<tr>
<td>8.</td>
<td>0.713:1</td>
<td>0.54</td>
<td>60</td>
<td>120</td>
<td>2.0</td>
<td>0.14</td>
</tr>
<tr>
<td>9.</td>
<td>0.713:1</td>
<td>0.36</td>
<td>60</td>
<td>60</td>
<td>5.6</td>
<td>0.61</td>
</tr>
<tr>
<td>10.</td>
<td>0.713:1</td>
<td>0.36</td>
<td>60</td>
<td>90</td>
<td>7.9</td>
<td>0.85</td>
</tr>
<tr>
<td>11.</td>
<td>0.713:1</td>
<td>0.36</td>
<td>60</td>
<td>150</td>
<td>5.0</td>
<td>0.53</td>
</tr>
<tr>
<td>12.</td>
<td>0.336:1</td>
<td>0.36</td>
<td>60</td>
<td>120</td>
<td>16.3</td>
<td>1.7</td>
</tr>
<tr>
<td>13.</td>
<td>1.049:1</td>
<td>0.36</td>
<td>60</td>
<td>120</td>
<td>10.2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Reaction conditions:

Wool : 1 gm.
Water : 300 ml.
Table II

Effect of concentration of monomer (MA), molar ratio of [FAS] / [KPS], temperature and time upon FAS-KPS system initiated grafting onto wool.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.064 : 1</td>
<td>0.184</td>
<td>45</td>
<td>90</td>
<td>3.6</td>
<td>0.76</td>
</tr>
<tr>
<td>2.</td>
<td>0.336 : 1</td>
<td>0.184</td>
<td>45</td>
<td>90</td>
<td>7.4</td>
<td>1.5</td>
</tr>
<tr>
<td>3.</td>
<td>0.713 : 1</td>
<td>0.184</td>
<td>45</td>
<td>90</td>
<td>55.5</td>
<td>11.7</td>
</tr>
<tr>
<td>4.</td>
<td>1.049 : 1</td>
<td>0.184</td>
<td>45</td>
<td>90</td>
<td>6.9</td>
<td>1.4</td>
</tr>
<tr>
<td>5.</td>
<td>0.713 : 1</td>
<td>0.184</td>
<td>45</td>
<td>30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6.</td>
<td>0.713 : 1</td>
<td>0.184</td>
<td>45</td>
<td>60</td>
<td>6.8</td>
<td>1.4</td>
</tr>
<tr>
<td>7.</td>
<td>0.713 : 1</td>
<td>0.184</td>
<td>45</td>
<td>120</td>
<td>41.6</td>
<td>8.7</td>
</tr>
<tr>
<td>8.</td>
<td>0.713 : 1</td>
<td>0.184</td>
<td>45</td>
<td>150</td>
<td>61.9</td>
<td>12.8</td>
</tr>
<tr>
<td>9.</td>
<td>0.713 : 1</td>
<td>0.184</td>
<td>30</td>
<td>150</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10.</td>
<td>0.713 : 1</td>
<td>0.184</td>
<td>60</td>
<td>150</td>
<td>72.6</td>
<td>15.2</td>
</tr>
<tr>
<td>11.</td>
<td>0.713 : 1</td>
<td>0.0368</td>
<td>60</td>
<td>150</td>
<td>3.5</td>
<td>3.7</td>
</tr>
<tr>
<td>12.</td>
<td>0.713 : 1</td>
<td>0.11</td>
<td>60</td>
<td>150</td>
<td>92.5</td>
<td>32.5</td>
</tr>
<tr>
<td>13.</td>
<td>0.713 : 1</td>
<td>0.257</td>
<td>60</td>
<td>150</td>
<td>70.3</td>
<td>10.5</td>
</tr>
<tr>
<td>14.</td>
<td>0.713 : 1</td>
<td>0.368</td>
<td>60</td>
<td>150</td>
<td>62.8</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Reaction conditions:

Wool : 1 gm.
Water : 300 ml.
**Table III**

Effect of total initial monomer (VAc) concentration upon percent grafting.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Initial conc. of monomer (VAc) in mols/litre</th>
<th>Initial rate of grafting (Rg) in %/minute</th>
<th>Induction period (Ip) in minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.106</td>
<td>0.166</td>
<td>27</td>
</tr>
<tr>
<td>2.</td>
<td>0.253</td>
<td>0.256</td>
<td>39</td>
</tr>
<tr>
<td>3.</td>
<td>0.36</td>
<td>0.470</td>
<td>59.5</td>
</tr>
</tbody>
</table>

a, Wool : 1 gm, Water : 300 ml, \( \frac{[FAS]}{[KPS]} : 0.713 : 1 

**Table IV**

Effect of total initial monomer (MA) concentration upon percent grafting

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Initial conc. of monomer (MA) in mols/litre</th>
<th>Initial rate of grafting (Rg) in %/minute</th>
<th>Induction period (Ip) in minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.11</td>
<td>2.09</td>
<td>87</td>
</tr>
<tr>
<td>2.</td>
<td>0.257</td>
<td>0.76</td>
<td>49.5</td>
</tr>
<tr>
<td>3.</td>
<td>0.368</td>
<td>0.74</td>
<td>42</td>
</tr>
</tbody>
</table>

b, Wool : 1 gm, Water : 300 ml, \( \frac{[FAS]}{[KPS]} : 0.713 : 1, \) Temp. : 60°C.
Table V
Physical Characterization of Wool

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Parameter</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Moisture content</td>
<td>16.0</td>
</tr>
<tr>
<td>2.</td>
<td>Acetone soluble fraction</td>
<td>7.06</td>
</tr>
<tr>
<td>3.</td>
<td>Ash content</td>
<td>1.66</td>
</tr>
</tbody>
</table>

Table VI
Solubility behaviour of wool and grafted wool

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample</th>
<th>Percent solubility</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.1N NaOH 4M HCl Oxidizing Urea bisulfite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>Wool</td>
<td>20.7</td>
<td>10.7</td>
<td>12.6</td>
<td>12.8</td>
</tr>
<tr>
<td>2.</td>
<td>W-g-Poly(MA)</td>
<td>10.6</td>
<td>10.7</td>
<td>51.8</td>
<td>1.7</td>
</tr>
<tr>
<td>3.</td>
<td>W-g-Poly(VAc)</td>
<td>9.16</td>
<td>8.12</td>
<td>1.25</td>
<td>5.64</td>
</tr>
</tbody>
</table>
PLOT OF PERCENT GRAFTING OF MA Vs TIME

Fig. 1

- ▲ ▲ [M]=0.11 mole / litre
- • • [M]=0.257 mole / litre
- ○ ○ [M]=0.368 mole / litre

TIME IN MINUTES
PLOT OF PERCENT GRAFTING OF VA\textsubscript{C} Vs TIME

- $[M] = 106$ mole / litre
- $[M] = 253$ mole / litre
- $[M] = 36$ mole / litre

Fig. 2
FIG. 3. INFRARED SPECTRUM OF WOOL-g-POLY(VAC).
Fig. 6
SCANNING ELECTRON MICROGRAPH OF PURE WOOL.
MAGNIFICATION : 1600 Times.

Fig. 7
SCANNING ELECTRON MICROGRAPH OF WOOL-g-
CHAPTER 6

GRAFTING OF VINYL MONOMERS ONTO REDUCED WOOL
BY USING POTASSIUM PERSULPHATE - FERROUS
AMMONIUM SULPHATE (KPS-FAS) SYSTEM
AS REDOX INITIATOR
INTRODUCTION

Wool contains disulfide linkages in addition to numerous other functional groups. Lipson and coworkers\(^\text{(78,79)}\) were the first to show that the polymerization of vinyl monomer is initiated on the wool molecule in the presence of a ferrous ion hydrogen peroxide redox system as a result of the formation of RS\(^*\) radical derived from initial attack at the disulfide bond. In 1949 Lipson\(^\text{(79)}\) reported graft copolymerization in wool through -SH formed by reduction of cystine in the wool protein. The probable role of cysteine in the polymerization was investigated further by Lipson and Hope\(^\text{(78)}\). It was observed that methacrylic acid polymerizes in presence of cysteine and ammonium persulfate. Thus, wool which contains cysteine with its easily reduced -S-S- linkage, can take part in forming suitable redox system for polymerization.

Lipson and Speakman\(^\text{(80)}\) reported the polymerization of methacrylic acid in wool which previously had been impregnated with a dilute solution of ferrous ammonium sulfate and dried. Polymerization was reported to proceed best at low pH, in the absence of oxygen and in the presence of traces of hydrogen peroxide.

Recently Schöberl and Wagner\(^\text{(81)}\) has further pointed out the role of the -SH in the reaction and elaborated the mechanism. Wool was reduced with thioglycolate and subsequently treated with alkyl halides. Graft copolymerization was carried ou
in presence of acrylonitrile and methacrylic acid. It was observed that alkylation of the -SH in the reduced protein prevents the formation of graft. However, in the presence of reduced wool (not alkylated), containing a protein -SH, polymerization proceeded at a faster rate than in the presence of untreated wool.

Proofs of the reaction with protein sulfur was found in the isolation of S- (beta-carboxy) propyl cysteine after treatment of reduced wool with methacrylic acid. Schoberl and Wagner \(^{(81)}\) however found that the reduced wool, where practically all the -S-S- bridges were reduced to -SH, merely added a molecule of monomer onto the -SH group but did not show evidence of graft polymerization at this site. They concluded, therefore, that the bulk of the polymer formed in this instance was not grafted.

Madras and Speakman \(^{(22)}\) have used persulfate alone to initiate the deposition of polymer on wool. Polymerization is initiated by the free radicals which are formed by the action of KPS on the cystine disulfide bond. They have suggested the following mechanism for grafting onto reduced wool.

\[
\text{RSH} \rightarrow \text{RS}^- + \text{H}^+ \quad \text{(a)}
\]

\[
\text{RS}^- + \text{S}_2\text{O}_8^{2-} \rightarrow \text{RS} + \text{SO}_4^{2-} + \text{SO}_4^-
\quad \text{(b)}
\]

\[
\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \cdot\text{OH} \quad \text{(c)}
\]
RS', SO₄⁻ or OH⁻ may initiate polymerization onto reduced wool.

Graft copolymerization of MMA onto wool and modified wool using ceric sulfate as the redox initiator has been studied by Kantouch and coworkers (82). It was observed that the percentage of grafting decreases by increasing the extent of reduction and it was lesser than the corresponding values of the untreated wool.

Further it was noted that when the reduction of wool is carried out in presence of Thioglycolic acid (TGA) (83) the cleavage of disulfide linkage to give thiol groups takes place in the following manner.

\[
\text{CH}_2\text{CH}_2\text{S-SCH}_2\text{CH}_2\text{CH} + 2\text{HSCOH}_2\text{COOH} \xrightarrow{\text{2 CHCH}_2\text{SH} + (-S\text{CH}_2\text{COOH})_2}
\]

The extent of reduction as shown by the cystine content of wool is dependent on pH (84). The amount of cystine reduced increases considerably as the pH increases but within pH range 2-6, it is found to be almost constant. The breaking of these cross linkages diminishes the strength of the fiber and it has been observed that the wet strength of the fiber can be reduced to one tenth (85) upon reduction by TGA. However, the original strength of the fiber can be restored by oxidation (86) of the reactive thiol group back to the disulfide linkage.
Various reagents that can be used to effect cross linking in wool through the agency of thiol groups, are:

1. **Ethylene dibromide**:
   \[
   2 \text{CH}_2 \text{CH}_2 \text{SH} + \text{BrCH}_2 \text{CH}_2 \text{Br} \rightarrow \text{CH}_2 \text{SCH}_2 \text{CH}_2 \text{SCH}_2 \text{Br}
   \]

2. **Benzoquinone**:
   The reaction of Benzoquinone with reduced wool is as follows:

3. **N,N'-Methylene bis acrylamide** (MBA):
   With (MBA), the sulfhydryl groups of reduced wool may react to give a product, on which two untreated vinyl groups are introduced for each disulfide link reduced.
Second possibility is that a bis thio ether bridge is formed in which the sulfhydryl groups have added to the same molecule of MBA.

The evidence that the cross linkage has occurred to some extent can be noted from greatly reduced solubility of the treated wool samples in alkali, as compared to the control and other vinylated wool samples. A marked reduction of supra contraction (5% NaHSO$_3$ at 95°C) of the treated fabric further adds to evidence in favour of cross linkage.
The break down of the disulfide group is symmetrical in presence of cupric ions. Wool treated at room temperature with a solution of 0.02 M cuprammonium hydroxide, 0.05M Na₂SO₃ and 8M urea at pH 9.8 - 10.5 will dissolve upto 90% in a few days. The reaction can be written as follows:

\[
\begin{align*}
S - S^- + 2Cu^{+2} + 2SO_3^{2-} &\rightarrow S^- - SO_3^- + S - S^- \\
R - SH + 2Cu^{+2} + SO_3^{2-} &\rightarrow R - S - SO_3^- + 2Cu^{+} + R^+
\end{align*}
\]

Reduction of cystine to cysteine can also be carried out in presence of sodium hydrosulfite but few studies are reported on grafting of vinyl monomers onto sodium hydrosulfite treated wool. Reduction of wool by NaHSO₃ has been extensively studied. Dilute solutions of NaHSO₃ donot react but most stringent conditions cause 50% of the cystine to be reduced giving the thiol compound and a sulfonate of cystine.

\[
\begin{align*}
\text{CO} & \text{CO} \\
\text{CH - CH}_2 - S - S - \text{CH}_2 & \text{CH} + \text{NaHSO}_3 \rightarrow \text{CH - CH}_2\text{SH} \\
\text{NH} & \text{NH}
\end{align*}
\]

\[
\begin{align*}
+ \text{NaO}_2\text{SCH}_2 - \text{CH} & \text{NH}
\end{align*}
\]

In this chapter, an attempt has been made to study the grafting of vinyl acetate (VAc) and methyl acrylate (MA) on reduced wool in presence of (KPS - FAS) system. The wool was reduced with sodium bisulfite. The purpose of present study is to ascertain the role of -SH groups in grafting of vinyl monomers onto wool.
EXPERIMENTAL

Materials and Method:

Himachali wool was purified by the same method as described in chapter 5. Monomers, Methyl acrylate (BDH) and vinyl acetate (BDH) were purified by distillation method described in chapter 1.

Potassium persulfate (KPS)(BDH) was used as received and Ferrous ammonium sulfate (FAS)(BDH) was purified by recrystallization from water.

Sodium bisulfite (BDH) was used as received. Pure and dry nitrogen gas was used in all experiments and purification was carried out by the method described in chapter 1.

Reduction:

One gram of wool was immersed in a solution of sodium bisulfite of various concentrations (0.5%, 1.0% and 1.5%) for 24 hours, 48 hours and 72 hours. The wool was then washed several times with water and methanol. The dried and weighed wool was then used in the grafting experiments. Optimum conditions for reduction were found from the experiments reported in tables I and II and these conditions were used for all other grafting experiments.

Graft copolymerization:

Graft copolymerization was carried out by the method discussed in chapter 5. Percentage and efficiency of grafting were calculated by method described in chapter 5.
Evidence of grafting:

Evidence of grafting of VAc and MA onto reduced wool was obtained by the same methods reported in chapter 5.
RESULTS AND DISCUSSION

Tables III and IV show the results of various parameters that influence grafting of Poly(VAc) and Poly(MA) onto reduced wool. Maximum grafting of MA occurred when reduction of wool was carried out with 1.0% NaHSO₃ for 24 hours. However, in case of VAc, maximum grafting was obtained when the reduction of wool was carried out with 0.5% NaHSO₃ for 24 hours.

Reduction of wool has been found to increase the number of thiol groups due to the cleavage of disulfide linkage in wool. The additional -SH groups generated upon reduction of wool provided extra sites for grafting.

The mechanism of grafting of Poly(VAc) and Poly(MA) in presence of (KPS-FAS) system is essentially the same as discussed for untreated wool (eqs. 1-8) in chapter 5.

However, when wool is reduced by NaHSO₃ solution, the generation of free radicals, 'OH and SO₄⁻⁻ are increased due to formation of additional thiol groups (eq. a-c), (page no. ).

Hydrogen abstraction from thiol groups may generate active sites onto reduced wool (eqs. e and f).

\[
RSH + \cdot OH \rightarrow RS' + H₂O \quad \text{(e)}
\]
\[
RSH + SO₄⁻⁻ \rightarrow RS' + HSO₄⁻⁻ \quad \text{(f)}
\]

Cross linking reaction can also occur between thiol radicals present in a favoured conformation.

\[
RS' + \cdot SR \rightarrow R - S - S - R
\]
In presence of monomer, addition of thiol to monomer probably occurs through free radical reactions as found for styrene by Kharash and coworkers\(^{(91,92)}\) (eqs. g,h).

\[
\begin{align*}
RS' + CH_2 &= CR_1R_2 \rightarrow RSCH_2 - CR_1R_2 & \text{(g)} \\
RSCH_2 - CH_4R' & + RSH \rightarrow RSCH_2CHR_1R_2H & + RS' & \text{(h)}
\end{align*}
\]

Thus it is expected that reduction of wool should enhance graft formation in presence of radical initiator. When FAS is added to KPS, following redox reaction occurs.

\[
\begin{align*}
Fe^{+2} + O_3SOO^- & + SO_3^- \rightarrow Fe^{+3} + SO_4^{2-} & + SO_4^- \\
SO_4^{2-} & + H_2O \rightarrow HSO_4^- & + 'OH
\end{align*}
\]

'OH and SO_4^{2-} may participate in chain transfer reaction with RSH to give additional active sites where grafting can occur.

Tables I and II show that maximum grafting of MA and VAc occurred to the extent of (78.5\%) and (22.3\%) when grafting was carried out onto wool treated with 1\% NaHSO_3 and 0.5\% NaHSO_3 solution, respectively for 24 hours. Under the same conditions, the untreated wool afforded maximum grafting of MA and VAc to the extent of (61.9\%) and (12.5\%), respectively. The increase in graft yield in the case of treated wool is due to additional -SH groups formed upon reduction. It is also observed from tables I and II
that the extent of reduction influences grafting. When the reduction time is increased from 24 hours to 48 or 72 hours, percent grafting decreases. Also when wool is reduced with more concentrated \( \text{NaHSO}_3 \) solution percent grafting decreases. These may indicate that upon prolonged treatment with more concentrated \( \text{NaHSO}_3 \) solution, some of the reducing agent is trapped in fiber matrix which then participates in forming a three component \((\text{Fe}^{+2} - \text{KPS} - \text{NaHSO}_3)\) redox system. This redox system is more effective in producing homopolymers with consequent decrease in graft yield. During grafting of wool treated with much higher concentration of \( \text{NaHSO}_3 \) solution for prolonged period large amount of homopolymer was observed.

**Effect of Monomer concentration**:

Tables III and IV show that with increase in concentration of VAc, percent grafting increases and reaches a maximum value (22.3 %) at a monomer concentration of 0.18 mole/litre. Beyond this concentration percent grafting decreases. This behaviour of VAc is consistent with its poor reactivity towards free radicals. With increase in monomer (VAc) concentration, side reactions are accelerated, resulting in decrease in percent grafting. It may be mentioned that VAc afforded higher percent grafting with unreduced wool than reduced wool under optimum conditions. This may indicate that additional -SH groups that are formed upon reduction, act as chain transfer agents towards donor monomer VAc resulting in the decrease of percent grafting.
With MA the situation is different. With increase in concentration of MA the percent grafting increases and reaches a maximum value (105.6) at a monomer concentration of 0.368 mole/litre. This would be expected since MA is highly reactive towards free radical and is not wasted in side reactions. It is also observed that reduced wool afforded higher percent grafting of MA than unreduced wool. This indicates that -SH groups play a significant role in promoting grafting of acceptor monomer MA in presence of KPS-FAS initiating system.

**Effect of Temperature:**

To obtain the optimum temperature for maximum grafting of VAc and MA onto reduced wool, graft copolymerization reactions were carried out at 30°, 45° and 60° C. Tables III and IV show that with increase in temperature, the percentage of grafting increases and reaches a maximum value at 60° C, beyond which the percent grafting starts decreasing due to preferential formation of homopolymer.

**Effect of Time:**

Tables III and IV show that the percentage of grafting increases with increase in time. Maximum percent grafting in case of MA and VAc was obtained within 150 and 120 minutes respectively after which it levelled off.
Molar Ratio of $\frac{[FAS]}{[KPS]}$

It can be seen from tables III and IV that the molar ratio $\frac{[FAS]}{[KPS]}$ plays a significant role in effecting entage and efficiency of grafting. Maximum percentage ing of both VAc and MA onto reduced wool occurred at molar ratio = 0.713 : 1. Same observation was ed in case of grafting of VAc and MA onto untreated discussed in chapter 5.
### Table I

Effect of extent of reduction on Graft copolymerization of VAc onto wool.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Time for reduction in hours</th>
<th>Conc. of NaHSO₃ solution</th>
<th>% age</th>
<th>% age Grafting Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>24</td>
<td>0.5%</td>
<td>22.3</td>
<td>4.8</td>
</tr>
<tr>
<td>2.</td>
<td>24</td>
<td>1.0%</td>
<td>9.4</td>
<td>2.0</td>
</tr>
<tr>
<td>3.</td>
<td>24</td>
<td>1.5%</td>
<td>4.2</td>
<td>0.9</td>
</tr>
<tr>
<td>4.</td>
<td>48</td>
<td>0.5%</td>
<td>2.0</td>
<td>0.4</td>
</tr>
<tr>
<td>5.</td>
<td>48</td>
<td>1.0%</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>6.</td>
<td>48</td>
<td>1.5%</td>
<td>4.7</td>
<td>1.0</td>
</tr>
<tr>
<td>7.</td>
<td>72</td>
<td>0.5%</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>8.</td>
<td>72</td>
<td>1.0%</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>9.</td>
<td>72</td>
<td>1.5%</td>
<td>4.7</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Reduced Wool: 1 g. Water: 300 ml. Temp.: 60°C. [VAc]: 0.18 mole/litre. Time: 120 minutes. [RAS]/[KPS]: 0.719:1

### Table II

Effect of extent of reduction on Graft copolymerization of MA onto wool.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Time for reduction in hours</th>
<th>Conc. of NaHSO₃ solution</th>
<th>% age</th>
<th>% age Grafting Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>24</td>
<td>0.5%</td>
<td>60.6</td>
<td>12.7</td>
</tr>
<tr>
<td>2.</td>
<td>24</td>
<td>1.0%</td>
<td>78.5</td>
<td>16.5</td>
</tr>
<tr>
<td>3.</td>
<td>24</td>
<td>1.5%</td>
<td>66.3</td>
<td>13.9</td>
</tr>
<tr>
<td>4.</td>
<td>48</td>
<td>0.5%</td>
<td>37.3</td>
<td>7.8</td>
</tr>
<tr>
<td>5.</td>
<td>48</td>
<td>1.0%</td>
<td>53.7</td>
<td>11.3</td>
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<td>6.</td>
<td>48</td>
<td>1.5%</td>
<td>66.6</td>
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<td>0.5%</td>
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<td>72</td>
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<td>12.5</td>
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<tr>
<td>9.</td>
<td>72</td>
<td>1.5%</td>
<td>65.4</td>
<td>13.7</td>
</tr>
</tbody>
</table>

Reduced Wool: 1 g. Water: 300 ml. Temp.: 60°C. [MA]: 0.184 mole/litre. Time: 150 minutes. [RAS]/[KPS]: 0.719:1
Table III

Effect of concentration of monomer, VAC and molar ratio of $[\text{FAg}/[\text{KPS}]]$, time and temperature upon KPS-FAS system initiated grafting of Poly (VAC) onto reduced wool

<table>
<thead>
<tr>
<th>S. No.</th>
<th>FAS/KPS</th>
<th>Conc. of monomer in mole/litre</th>
<th>Temp. $^\circ$C</th>
<th>Time in minutes</th>
<th>% age Grafting</th>
<th>% age Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.713 : 1</td>
<td>0.18</td>
<td>30</td>
<td>120</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.</td>
<td>0.713 : 1</td>
<td>0.18</td>
<td>45</td>
<td>120</td>
<td>7.6</td>
<td>1.6</td>
</tr>
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<td>3.</td>
<td>0.713 : 1</td>
<td>0.18</td>
<td>60</td>
<td>120</td>
<td>22.3</td>
<td>4.8</td>
</tr>
<tr>
<td>4.</td>
<td>0.713 : 1</td>
<td>0.18</td>
<td>60</td>
<td>45</td>
<td>7.3</td>
<td>1.1</td>
</tr>
<tr>
<td>5.</td>
<td>0.713 : 1</td>
<td>0.18</td>
<td>60</td>
<td>90</td>
<td>11.9</td>
<td>2.5</td>
</tr>
<tr>
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<td>0.713 : 1</td>
<td>0.18</td>
<td>60</td>
<td>150</td>
<td>19.5</td>
<td>4.2</td>
</tr>
<tr>
<td>7.</td>
<td>0.713 : 1</td>
<td>0.18</td>
<td>60</td>
<td>120</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8.</td>
<td>0.713 : 1</td>
<td>0.253</td>
<td>60</td>
<td>120</td>
<td>4.7</td>
<td>0.7</td>
</tr>
<tr>
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<td>0.713 : 1</td>
<td>0.253</td>
<td>60</td>
<td>120</td>
<td>1.3</td>
<td>0.2</td>
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<tr>
<td>10.</td>
<td>0.336 : 1</td>
<td>0.18</td>
<td>60</td>
<td>120</td>
<td>1.5</td>
<td>0.3</td>
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<tr>
<td>11.</td>
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<td>0.18</td>
<td>60</td>
<td>120</td>
<td>2.8</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Reaction conditions:

- Reduced wool : 1 gm.
- Water : 300 ml.
### Table IV

Effect of concentration of monomer MA and molar ratio, of \( \text{FAS} / \text{KPS} \) time and temperature upon KPS-EAS system initiated grafting of Poly MA onto reduced wool

<table>
<thead>
<tr>
<th>S.No.</th>
<th>( \frac{\text{FAS}}{\text{KPS}} )</th>
<th>Conc. of monomer in moles/litre</th>
<th>Temperature ( \degree C )</th>
<th>Time in minutes</th>
<th>% age Grafting</th>
<th>% age Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.713 : 1</td>
<td>0.184</td>
<td>60</td>
<td>45</td>
<td>43.8</td>
<td>9.2</td>
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<td>0.0</td>
</tr>
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<td>150</td>
<td>5.0</td>
<td>1.05</td>
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<td>8.</td>
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<td>60</td>
<td>150</td>
<td>27.0</td>
<td>9.5</td>
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<tr>
<td>9.</td>
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<td>150</td>
<td>82.6</td>
<td>12.4</td>
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<td>105.6</td>
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<td>150</td>
<td>25.1</td>
<td>2.6</td>
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<tr>
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<td>150</td>
<td>24.5</td>
<td>2.57</td>
</tr>
</tbody>
</table>

**Reaction conditions:**

- Reduced wool: 1 gm.
- Water: 300 ml.
REFERENCES


2. E. Fischer, Ber., 35, 1095 (1902).


36. L. Valentine, ibid., 47 T 1 (1956).
63. Kolthoff, Medalia and Raaen, ibid 73, 1733 (1951).
64. Fordham and Williams ibid p.4855.
65. Merz and Waters, Gmelin’s Hand buch der Anorganischen chemie, 13 97, 161, 235 Bor (1954).
70. Berry and Peterson, ibid., 73, 5195 (1951).
90. Ibid., 32, 837 (1938).