# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Fundamental of Polymerization

### 2.1.1 Definitions

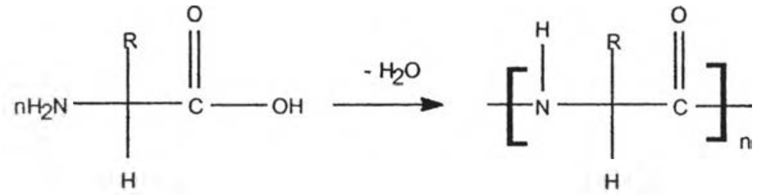
Many of the terms and definition used in polymer chemistry are not encountered in conventional textbooks, and for this reason the following summary of terminology is given.

#### Monomers

A monomer is any substance that can be converted into a polymer. For example, ethylene is a monomer that can be polymerized to polyethylene.

$$nCH_2{=}CH_2 \longrightarrow \left[ CH_2-CH_2 \right]_n$$

An amino acid is a monomer, which can polymerize to polypeptide (by loss of water)



$$nH_2N-\overset{R}{\underset{H}{|}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{-H_2O} \left[\overset{H}{\overset{|}{N}}-\overset{R}{\underset{H}{|}}-\overset{O}{\overset{\|}{C}}\right]_n$$

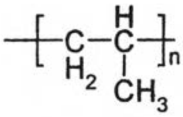
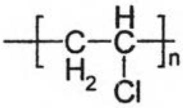
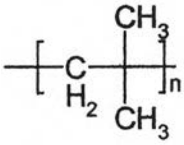
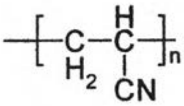
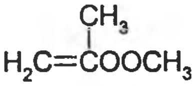
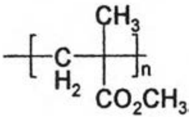
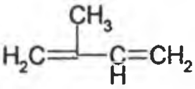
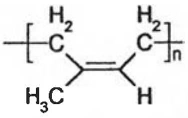
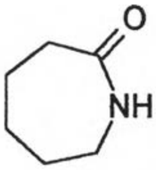
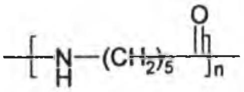
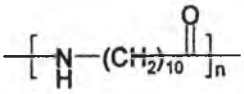
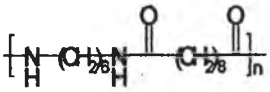
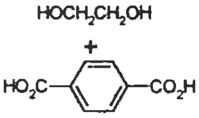
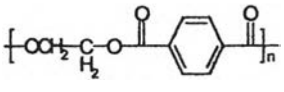
#### Dimers, Trimers and Oligomers

Two monomer molecules react together to form a dimer. The dimer reacts with a third monomer to yield a trimer and so on (tetramers, pentamers...). Low-molecular-weight polymerization products, for example, dimers,trimers, tetramers and so on are known as oligomers. Same care should be taken to avoid use of the term "polymer" to describe materials that are really oligomers became these two types of products have very different properties.

#### Polymers

The term polymer is used to describe high-molecular-weight substance. However, this is very board definition to divide polymers into subcategories according to their molecular weight and structure. A better definition might be base on the member of repeating units in the structure.

Table 2.1 Repeating unit of polymer(3)

| Monomer structure | Monomer name | Polymer repeating unit | Source name | IUPAC name |
|---|---|---|---|---|
| $CH_3CH=CH_2$ | Propylene |  $\left[ \underset{H_2}{C}-\underset{CH_3}{\overset{H}{C}} \right]_n$ | Polypropylene | Poly(propylene) |
| $H_2C=CHCl$ | Vinyl chloride |  $\left[ \underset{H_2}{C}-\underset{Cl}{\overset{H}{C}} \right]_n$ | Poly(vinyl chloride) | Poly(1,1-chloroethylene) |
| $H_2C=C(CH_3)_2$ | Isobutylene |  $\left[ \underset{H_2}{C}-\underset{CH_3}{\overset{CH_3}{C}} \right]_n$ | Polyisobutylene | Poly(1,1-dimethylethylene) |
| $H_2C=CHCN$ | Acrylonitrile |  $\left[ \underset{H_2}{C}-\underset{CN}{\overset{H}{C}} \right]_n$ | Polyacrylonitrile | Poly(1-cyanoethylene) |
|  $H_2C=\overset{CH_3}{C}OOCH_3$ | Methyl methacrylate |  $\left[ \underset{H_2}{C}-\underset{CO_2CH_3}{\overset{CH_3}{C}} \right]_n$ | Poly(mehyl methacrylate) | Poly[1-(methoxycarbonyl)-1-methylethylene] |
|  | Isoprene |  | cis-1,4-Polyisorene | cis-Poly(1-methyl-1-butenylene) |
|  | Caprolactam |  | Polycaprolactam or nylon 6 | Poly[imino((1-oxohexametylene)] |
| $H_2N(CH_2)_{10}CO_2H$ | 11-Aminoundecanoic acid |  | Poly(11-undecanoamide) or nylon11 | Poly[imino(1-imino)1-oxoundeca-methylene)] |
| $H_2N(CH_2)_6CO_2H$<br>+<br>$HO_2C(CH_2)_8CO_2H$ | Hexamethylenediamine<br>+<br>Sebacic acid |  | Poly(hexamethylene sebacamide) or nylon 6,10 | Poly(iminohexamethylene-iminosebacoyl) |
|  | Ethylene glycol<br>+<br>terephthalic acid |  | Poly(ethylene terephthalate) | Poly(oxyethylene-oxyterephthaloyl) |

### 2.1.2. Types of Polymerization

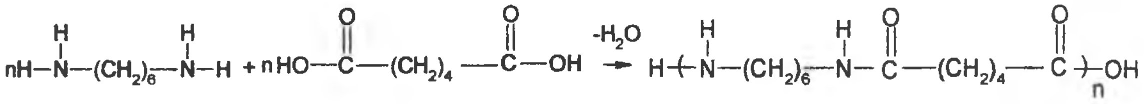
Traditionally, polymer has been classified into two main groups, condensation polymers and addition polymers. This classification, first proposal by Carothers, is based on whether the repeating unit of the polymer contains the same atoms as the monomer. Addition polymer has the same atoms as the monomer in its repeating unit, whereas condensation polymers contain fewer because of the formation of by products during the polymerization process. The corresponding polymerization processes would then be called addition polymerization and condensation polymerization.

In more recent years the emphasis has changed to classifying polymers according to whether the polymerization occurs in a stepwise fashion (step reaction or step growth) or by propagating from a growing chain (chain reaction or chain growth)

### 2.1.2.1 Condensation or Step-Reaction Polymerization

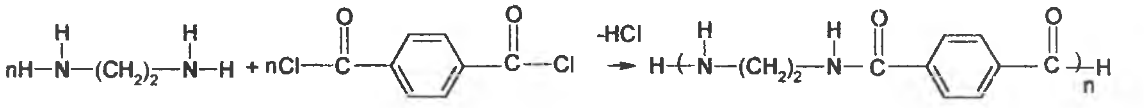
This type of polymerization is reactions that monomer molecules react to release a small molecule such as water, alcohol, and hydrochloric acid.

For example:



$$n\mathrm{H}-\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-(\mathrm{CH_2})_6-\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\mathrm{H} + n\mathrm{HO}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-(\mathrm{CH_2})_4-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH} \xrightarrow{-\mathrm{H_2O}} \mathrm{H}\left(\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-(\mathrm{CH_2})_6-\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-(\mathrm{CH_2})_4-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\right)_n\mathrm{OH}$$

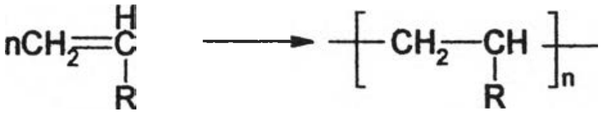
Hexamethylene diamine Adipic acid Nylon6,6



Ethylene diamine Terephthaloyl chloride poly(ethylene terepthalamide)

### 2.1.2.2 Addition or Chain Growth Polymerization

Great many synthesis polymers are prepared by the polyaddition reactions of unsaturated organic compounds. In general terms, such polymerization can be described by the scheme shown in reaction.



Such reactions can be induced either by the addition of free-radical forming reagents or by ionic initiators so called free-radical polymerization and ionic polymerization.

Free-Radical Polymerization

In a free-radical addition polymerization, the growing chain end bears an unpaired electron. Addition of each monomer molecule to the chain end involves an attack by the radical site on the unsaturated monomer. Thus, the unpaired electron is transferred to the new chain end at each addition step.

Free-radical polymerization is chain reaction. The addition of a monomer molecule to an active chain end regenerates the active site at the chain end. Hence, a large number of monomer molecules are consumed for each active site introduced into the system. In chain-reaction polymerization we may recognize for distinct types of processes. They are:

1. Chain initiation -a process in which highly reactive transient molecules or active centers are formed
2. Chain propagation -the addition of monomer molecules to the active chain end, accompanied by regeneration of the terminal active site.
3. Chain transfer -involving the transfer of the active site to another molecules (e.g., monomer). The molecule that has lost the active site is now "dead" from a chain-propagation point of view. The molecule that has accepted the active site can start a new chain.
4. Chain termination -a reaction in which the active chain centers are destroyed chain reaction are found in free-radical, anionic and cationic vinyl-type polymerization. In free-radical processes all of the four steps listed above can usually be identified.

Schematically, a free-radical polymerization sequence can be represented by the reactions shown in (1) to (7). In these equations:

$M$ represents a molecule of monomer

$R'^{\bullet}$ is an initiating free radical from the initiator

$R^{\bullet}_{n}$ is the propagating free radical with a degree of polymerization, n

$YZ$ is a chain transfer agent that may be solvent, monomer, initiator, or polymer molecules.

$P_n$ is the final inactive polymer.

$$\begin{array}{lll}
\left.\begin{array}{l}
\text{Initiator} \longrightarrow 2R'^{\bullet} \\
R'^{\bullet} + M \longrightarrow R^{\bullet}_{1}
\end{array}\right\} \text{Initiation} & & \begin{array}{r}(1)\\(2)\end{array} \\
\left.\begin{array}{l}
R^{\bullet}_{1} + M \longrightarrow R^{\bullet}_{2} \\
\cdots\cdots\cdots\cdots\cdots\cdots \\
R^{\bullet}_{n} + M \longrightarrow R^{\bullet}_{n+1}
\end{array}\right\} \text{Propagation} & & \begin{array}{r}(3)\\ \\(4)\end{array} \\
R^{\bullet}_{n} + YZ \longrightarrow R_{n}Y + Z^{\bullet} \quad \text{chain transfer} & & (5) \\
\left.\begin{array}{l}
R^{\bullet}_{n} + R^{\bullet}_{m} \longrightarrow P_{n+m} \\
R^{\bullet}_{n} + R^{\bullet}_{m} \longrightarrow P_{n} + P_{m}
\end{array}\right\} \text{Termination} & & \begin{array}{r}(6)\\(7)\end{array}
\end{array}$$

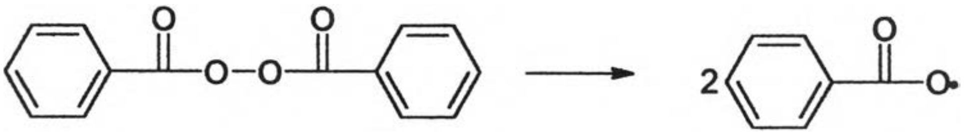
Free-Radical Initiators

Initiation of a free-radical polymerization requires the production of free radicals in presence of the unsaturated monomer. The types of initiators can be divided into four types: follow the alternative mechanisms that are available for initiation.

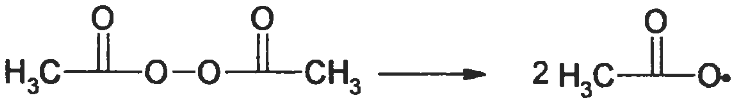
1.Thermal Decomposition of Initiators

This type is the most widely used made of generating radicals to initiate polymerization for both commercial polymerization and theoretical studies. Polymerization initiated in this manner is often referred to as thermal initiated or thermal catalyzed polymerization. The member of different types of compounds that can be used as thermal initiators is rather limited. One is usually limited to compounds with bond dissociation energies with dissociate too slowly or too rapidly. Only a few classes of compounds-including those with O-O, S-S, N-O bonds-possess the desired range of dissociation energies.

Several different types of peroxide compounds are widely used. These are acyl peroxides such as

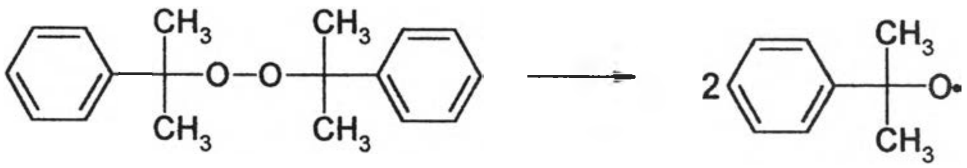


Benzoyl peroxide



Acetyl peroxide

Alkyl peroxides such as:



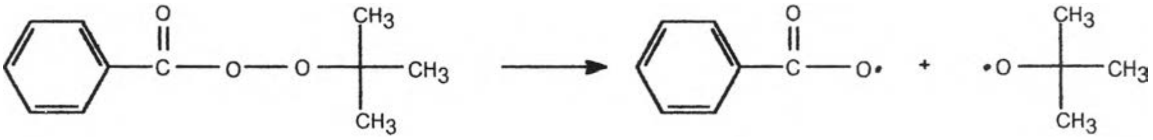
Cumyl peroxide

Hydroperoxides such as:

t-butyl hydroperoxide

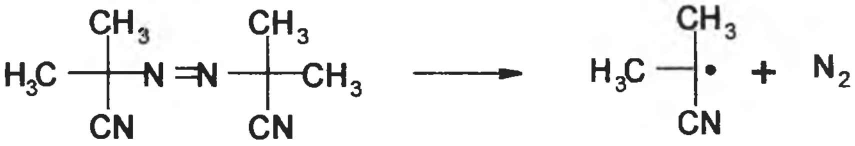
Cumyl hydroperoxide

Perester such as:



t-butyl perbenzoate

Aside from the various peroxy compounds, the main other class of compound used extensively, as initiators are the azo compounds. 2,2'-azobisisobutyronitrile (AIBN) is the most important member of this class of initiators, although other azo compound are also used.



2,2'-Azobisisobutyronitrile

Among other initiators that have been studied are disulfides

$$RS{-}RS \longrightarrow 2RS^{\bullet}$$

And terazenes

$$R_2N\text{-}N{=}N\text{-}NR_2 \longrightarrow 2R_2N^{\bullet} + N_2$$

The various initiators are used at different temperature depending on their rates of decomposition. Thus azobisisobutyronitrile (AIBN) is commonly used at 50-70$^0$C, benzoyl peroxide at 80-95$^0$C, and dicumyl or di-t-butyl peroxide at 120-140$^0$C

### 2.Redox Initiators

Many oxidation-reduction reactions produce radicals that can be used to initiate polymerization. This type of initiation is referred to as redox initiation. A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperatures, depending on and even lower. This allows a greater freedom of choice of the polymerization can be initiated photolytically as well as thermally. A wide ranges of redox reactions, including both inorganic and organic components either wholly or imparts, may be employed for this purpose.

### Types of Redox initiators

a) Peroxide in combination with a reducing agent are common source of radicals, for example, the reaction of hydrogen peroxide with ferrous ion

$$H_2O_2 \ + \ Fe^{2+} \longrightarrow HO^{-} \ + \ HO^{\bullet} \ + \ Fe^{3+}$$

Ferrous ion also promotes the decomposition of a variety of other compounds including various types of organic peroxides.

$$ROOR \xrightarrow{Fe2+} RO^{-} \ + \ RO^{\bullet} \ + Fe^{3+}$$

$$ROOH \xrightarrow{Fe2+} HO^{-} \ + \ RO^{\bullet} \ + Fe^{3+}$$

$$ROOCR' \xrightarrow{Fe2+} R'CO- \ + \ RO^{\bullet} \ + Fe^{3+}$$

Other reductants such as $Cr^{2+}$,$V^{2+}$,$Ti^{3+}$,$Co^{2+}$and $Cu^{2+}$ can be employed in place of ferrous ion in many instances.

b) The combination of a variety of inorganic reductants and inorganic oxidants initiated radical polymerization, for example,

$$-O_3S\text{-}O\text{-}O\text{-}SO_3- + Fe^{2+} \longrightarrow Fe^{3+} \ + SO^{2-}_4 + \ SO^{-\bullet}_4$$

$$-O_3S\text{-}O\text{-}O\text{-}SO_3- + S_2O_3^{2-} \longrightarrow SO^{2-}_4 + SO^{-\bullet}_4 + S_2O_3^{2-}$$

Other redox systems include reductants such as $HSO_3^-$, $SO_3^{2-}$, $S_2O_3^{2-}$ and $S_2O_5^{2-}$ in combination with oxidants such as $Ag^{2+}$, $Cu^{2+}$,$Fe^{3+}$,$ClO_3^-$ and $H_2O_2$

c) Organic-inorganic redox pairs initiate polymerization, usually but not always by oxidation of the organic component, for example, the oxidation of an alcohol by $Ce^{4+}$

$$\text{R-CH2-OH} + Ce^{4+} \longrightarrow Ce^{3+} + H^{+} + \text{R-CH-OH}$$

Or by $V^{5+}$, $Cr^{6+}$, $Mn^{3+}$

d) There are some initiator systems in which the monomer itself acts as one component of the redox pair. Examples are thiosulfate plus acrylamide of methacrylic acid and N, N-dimethylaniline plus methyl methacrylate.

3. Photo Chemical Initiators

Photochemical or photoinitiated polymerizations occur when radicals are produced by ultraviolet and visible light irradiation of a reaction system. In general, light absorption results in radical production by either of two pathways:

1. Some compound in the system undergoes excitation by energy absorption and subsequent decomposition into radicals.
2. Some compound undergoes excitation and the excited species interacts with a second compound (by either energy transfer or redox reaction) to form radicals derived from the latter and/or former compounds.

Photochemical polymerization has found applications in decorative and protective coating and inks for metal, paper, wood, and plastics; in photolithography for producing inter grated and printed circuits; and in curing dental materials.

4. Other Methods of Initiation

-Electroinitiation

Aqueous and various organic solvents (e.g., DMF, methylene chloride, and methanol) have been employed in the presence of various inorganic compounds. The latter are used either to conduct current or participate in the initiation process. Depending on the components present, radicals and/or ion are formed when current is passed through the reaction system, and this initiate polymerization. Such polymerzations are referred to as electroinitiated or electrolytic polymerization

-Plasma

Plasma polymerization occurs when a gaseous monomer is placed in an electric discharge at low pressures under conditions where plasma is created. Plasma consists of ionized gaseous molecules. In some cases, the system is heated and/or placed in a radio frequency field to assist in creating the plasma. A variety of organic molecules including alkennes, alkynes and alkanes undergo polymerization to high-molecular-weight products under these conditions. The propagation polymerization offers a potentially unique method of forming this polymer films for uses such as thin film capacitors, antireflection coatings, and various types of this membranes.

### Techniques of Free Radical Polymerization

Free radical polymerization can be accomplished in bulk, solution, suspension or emulsion. Ionic and other nonradical polymerization are usually confined to solution techniques. Each of the methods has advantages and disadvantages, as shown in Table 2.2. In addition, work has also been done on solid-and gas-phase polymerization means, in effect, bulk polymerization in which monomer vapors diffuse to the polymerization site.

Table 2.2 Free radical polymerization techniques

| Method | Advantages | Disadvantages |
|---|---|---|
| Bulk | Simple; no contaminants added | Reaction exotherm difficult to control; high viscosity |
| Suspension | Heat readily dispersed; low viscosity; polymer obtained in granular form and may be used directly | Washing and/or during required; agglomeration may occur; contamination by stabilizer. |
| Solution | Heat readily dispersed; low viscosity; may be used directly as solution | Added cost of solvent; solvent difficult to remove; possible chain transfer with solvent; possible environmental pollution. |
| Emulsion | Heat readily dispersed; low viscosity; high molecular weight obtainable; may be directly as emulsion; works on tacky polymers | Contamination by emulsifier and other ingredients; chain transfer agents often needed to control DP; washing and drying necessary for bulk polymer. |

Table 2.3 Commercially important vinyl polymers prepared by free radical polymerization [a] (3)

| Polymer of copolymer | Method of manufacture[b] | Major uses |
|---|---|---|
| Polyethylene, low density (LDPE) | HP, B, Sol | Packaging film, wire and cable insulation, toys, flexible bottles, house wares, coatings |
| Poly(vinyl chloride) | B, S, Sol, E | Construction, rigid pipe, flooring, wire and cable insulation, film and sheet |
| Polystyrene[c] | B, S, Sol, E | Packaging (foam and film), foam insulation, appliances, housewares, toys |

| | | |
|---|---|---|
| Styrene-butadiene rubber (SBR) | E | Tires, belting, flooring, molded goods, shoe soles, electrical insulation |
| Butadiene-acrylonitrile copolymer (nitrile rubber) | E | Fuel tanks, gasoline, hoses, adhesives, impregnated paper, leather and textiles |
| Acrylonitrile-butadiene-styrene copolymer (ABS) | E | Engineering plastics, household appliances, business machines, telephones, electronics, automotive parts, luggage |
| Polychloroprene (neoprene rubber) | E | Tires, wire coatings, belting, hoses, shoe heels, coated fabrics |
| Poly(methyl methacrylate) | B, S | Automotive parts, molding, compositions, decorative panels, skylights, glazing |
| Polyacrylonitrile | S | Textile fibers, food packaging |
| Poly(vinyl acetate) | B, S, Sol, E | Water-based paints, adhesives, conversion to poly(vinyl alcohol) |
| Poly(vinylindene chloride)[c] | E, S | Food packaging |
| Poly(acrylic acid) and poly(methacrylic acid) | Sol, E | Adhesives, thickening agents, ionomers |
| Polyacrylamide | E | Thickening agent, flocculent |
| Polytetrafluoroethylene | HP, S, Sol | Electrical insulation, gaskets, bearings, bushings, valves, nonstick cooking utensils |
| Polytrichlorofluoroethylene | S, Sol | Gaskets, tubing, wire insulation |
| Poly(vinylidene fluoride) | S, Sol | Protective coatings, gaskets, pipe |
| Poly(vinyl fluoride) | S, Sol | Protective coatings |
| Allyl resins[f] | B, Sol | Lenses, electronics parts |

[a] A number of copolymers are manufactured besides the high-volume ones listed.

[b] HP= high presusre; B = bulk; E = emulsion; S = suspension; Sol = solution.

[C] Poly(p-methylstyrene) also available.

[E] Including copolymers. Principally with vinyl chloride.

[F] Crosslinked diallyl and triallyl esters and ethers.

1) Bulk

Bulk polymerization is simplest from the standard point of formulation and equipment, but it is also the most difficult o control, particularly when the polymerization reaction is very exothermic. This, coupled with problems of heat transfer as the monomer-polymer solution increases in viscosity, limits the use of bulk methods in commercial production, although more efficient bulk processes have been developed in recent years.

The major commercial uses of bulk vinyl polymerization are in casting formulations and low-molecular-weight polymers for use as adhesives, plasticizers, tackifiers, and lubricant additives.

2) Suspension

Suspension polymerization involves mechanically dispersing monomer in a noncompatible liquid, usually water, and polymerizing the resultant monomer droplets by use of a monomer-soluble initiator. Monomer is kept in suspension by continuous agitation and the use of stabilizers such as poly(vinyl alcohol) or methyl cellulose. If the process is carefully controlled, polymer is obtained in the form of granular beads, which are easy to handle and can be isolated by filtration or by spraying into a heated chamber (spray drying). A major advantage that heat transfers very efficient and the reactions therefore easily controlled. Suspension polymerization cannot be used for tacky polymer such as elastomers because the tendency for agglomeration of polymer particles.

3. Solution

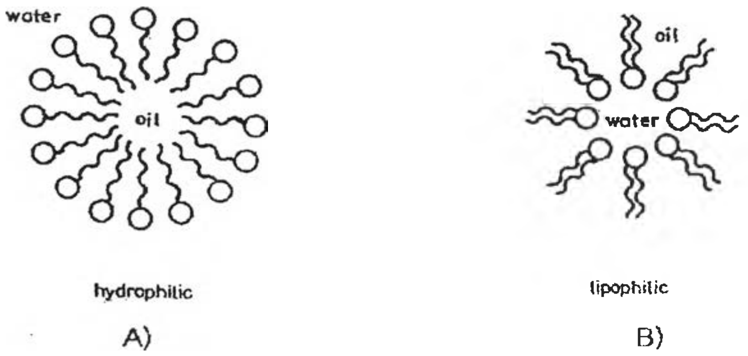
Like suspension, solution polymerization allows efficient heat transfer. Solvent must be chosen carefully, otherwise chain transfer reactions may severely limit the molecular weight. Because of problems in removing solvent completely from the resultant polymer, the method is best suited to applications where the solution may be used directly, as with certain adhesives or solvent -based paints.

4. Emulsion

Emulsion polymerization resembles suspension polymerization in that water is used as a dispersing medium and heat transfer is very efficient; but they're the similarity ends. Emulsifying agent such as soap or detergent disperses monomer in the aqueous phase. Initiator radicals, usually of the redox type, are generated in the aqueous phase and diffuse into soap micelles swollen with monomer molecules. As monomer is used up in the polymerization reaction, more monomer migrates into the micelles, and thus the reaction continuous. Termination of polymerization occurs by radical combination when a new radical diffuses into the micelle. Because only radical is present in the micelle prior to termination, extremely high molecular weights are obtainable generally too high to be of practical value unless compounds called chain transfer agents are added that control the degree of polymerization.

Emulsion polymerization is widely used in industry for large –scale preparations, and is practical useful for manufacturing water-based (latex) paints or adhesives in which the emulsified product is used directly. Emulsion polymerization is also suitable for preparing tacky polymer because the very small particles are stable and resist agglomeration.

The dispersed liquid-in-liquid systems, i.e. emulsion, can be prepared by strong agitation of the two mutually insoluble or only partially-soluble liquids together, usually oil (designation for a water-insoluble liquid) in water (classical, direct emulsions, o/w) or water-in-oil (inverse emulsion, w/o)



hydrophilic
A)

lipophilic
B)

Figure 2.1 A) micelle of oil-in-water emulsion, B) micelle of water-in-oil emulsion (5)

In the absence of an emulsion stabilizer, on interruption of the stirring, the macrophases gradually separate. Formation of a stable oil-in-water (o/w) or water-in-oil (w/o) emulsions not only determined by the character of the stabilizer (emulsifier) but also by the ratio of both macrophases. Emulsion prepared by stirring are usually dimensionally polydisperse, the dimensions of the droplets of the dispersed phase in the continuous phase being rather large, i.e. of the order of $10^4$ nm and more. The formation of an emulsion with droplet size below this limit requires high-intensity stirring, i.e. it requires large amounts of energy. This procedure is therefore disadvantageous if a high degree of dispersion of the emulsion particles is required. The use of a mixture of an ionic emulsifier and higher alkanol, in the presence of water and oil phases accompanied with the formation of the o/w emulsion provides a mean. The term miniemulsion has been proposed for these emulsions since the size of the dispersed particles of a miniemulsion (100-400 nm) lies between that of a conventional macroemulsion and that of microemulsion(5).

Microemulsions are colloidal dispersion of varying stability with dimensions: the dispersed phase from 5 to 100 nm(4). Microemulsions usually contain water, hydrocarbon solvent, surfactant, and co-surfactant. (usually $C_4$-$C_8$ n-alkanols).

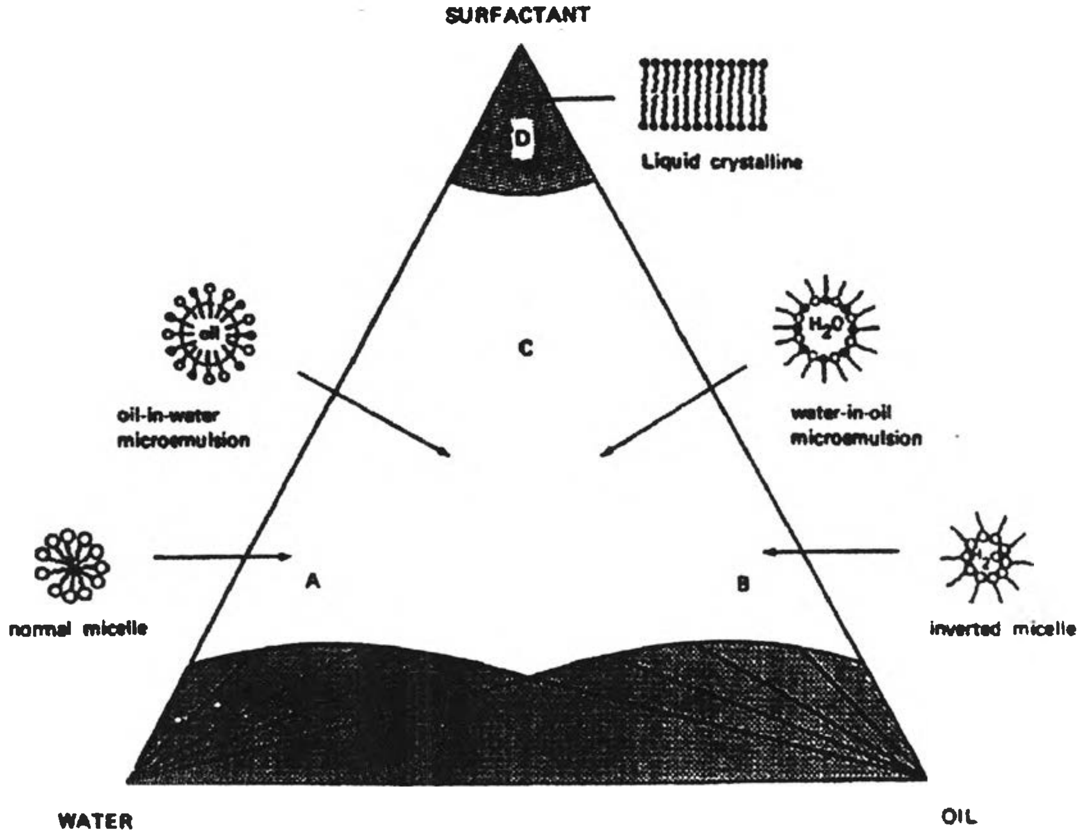


Figure 2.2 Schematic ternary-phase diagram of an oil-water-surfactant microemulsion system consisting of various associated microstructures. A, Normal micelles or o/w microemulsions; B, reverse micelles or w/o microemulsions; C, concentrated microemulsion domain; D, liquid crystal or gel phase. Shaded areas represent multiphase region$^{(6)}$.

The main role of co-surfactant was to reduce the interfacial tension to such low values.

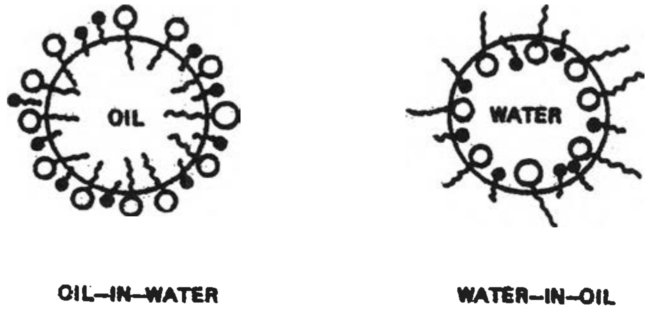


Figure 2.3 Schematic diagram for oil-in-water (o/w) and water-in-oil (w/o) microemulsion structures. The smaller molecules represent cosurfactant$^{(6)}$.

**Harkins' Theory**

Harkins assumes that the polymerization process starts with the decomposition of a water-soluble initiator such as $K_2S_2O_8$ into primary radical, which are absorbed into monomer-swollen emulsifier micelles. The propagation itself proceeds in side micelles. As reaction proceeds, the micelles become polymer/monomer particles; the concentration of micellar emulsifier and the formation of new particle end control their repeating unit when they are consumed. The monomer is presented in the system as monomer droplets from which it diffuses into the polymer particles and thus maintains dynamic equilibrium until the time at which the monomer droplets disappear. The droplets serve only as a reservoir of monomer. In parallel with the growth of the polymer particles and with the diffusion of monomer from the monomer droplets into the particles, the molecules of free emulsifier diffuse onto surface of the particles. The role of the emulsifier is to stabilize the polymer particles being formed and growing. After it is consumed, no further particles and the emulsifier absorbed on their surface are in dynamic equilibrium with the emulsifier dissolved in water. On consumption of the monomer droplets, the dynamic equilibrium is broken and the centers of polymerization are fed only with monomer present in the polymer particles. This is the micellar model and is shown in Fig 2.4

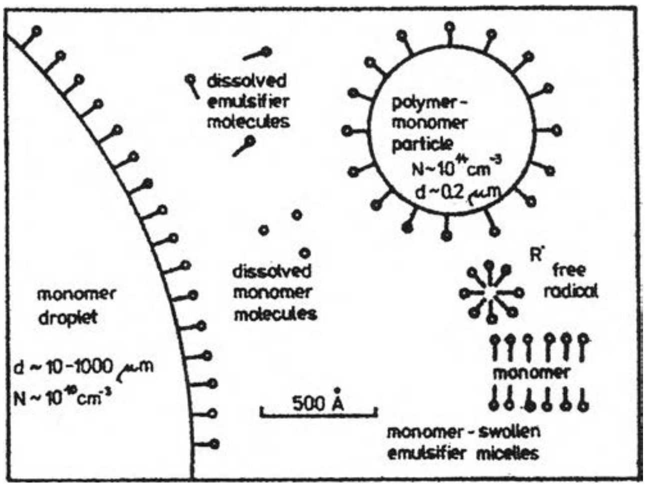


Figure 2.4 Harkins' micellar model of emulsion polymerization. Number of monomer molecules dissolved in water: ~$10^{-18}$ $cm^{-3}$, number of monomer –swollen emulsifier micelles: ~$10^{10}$ $cm^{-3}$.(5)

**Surfactants**

The word surfactant does not appear in most dictionaries. This is because it is not only a technical term, but also a diminutive form of the phrase **SURFace ACTive AgeNT**. Their molecular structure is amphiphilic (from the Greek amphi meaning "on both sides" and phileein meaning, " on both side"). The molecules have two distinct parts; one that has an affinity for the solvent and the other does not. In aqueous solutions, these two moieties are hydrophilic and hydrophobic, respectively. It is the tendency for the hydrophobic parts of the molecules to aggregate because of mutual dislike of the solvent, which is the driving force for surfactant self-association.

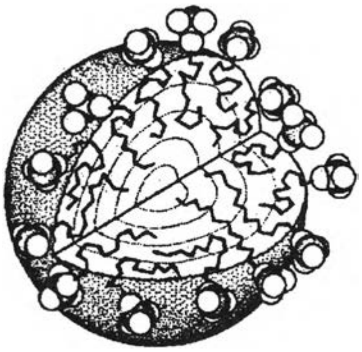
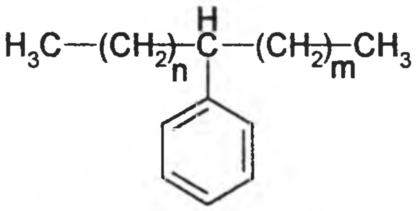
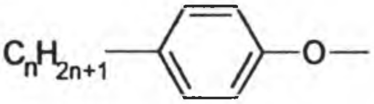
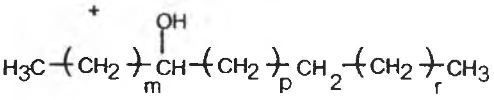
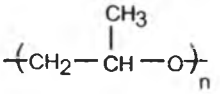


Figure 2.5 The detailed structure of micelle. The hydrocarbon chains of surfactants pack at liquid hydrocarbon density in the core and are almost as disordered as in the bulk liquid state.(7)

Micelles are composed mainly of amphiphiles, which are self-assembled into a bilayer structure with molecules oriented so that the hydrophilic group are on the outside of the membrane and the hydrophobic groups avoid contact with the aqueous regions by being packed closely together inside the membrane. A schematic drawing of a cross-section of a cell membrane can be seen above.

Surfactant consists of two parts; hydrophobic part is usually called the "tail part" and is most commonly a simple hydrocarbon group (Table 2.4). When soaps were the only detergents the tail would be a mixture of these alkyl groups occurring in the fatty acid derived from hydrolysis of natural fats and oils. These would be straight alkyl chains of length around $C_{12}$-$C_{20}$ with certain fraction of unsaturation depending on the source of the fat.

Table 2.4 Summary of hydrophobic groups of surfactant.(7)

| Group | Structure |
|---|---|
| Alkyl | $H_3C-(CH_2)_n-$ |
| Linear alkyl benzene |  |
| Alkylaryl (e.g. alkyl phenol) |  |
| α-Olefin | $H_3C-(CH_2)_n-CH=CH-$<br>+<br><br>$H_3C-(CH_2)_m-CH(OH)-(CH_2)_p-CH_2-(CH_2)_r-CH_3$ |
| Poly(propylene oxide) | <br>$-(CH_2-CH(CH_3)-O)_n-$ |

Hydrophilic part of a surfactant is usually referred to as the " head part" and is either strongly polar or charged. Where the charged group is anionic the counterion is usually $Na^+$ and for cationic surfactants the counterion is usually $Cl^-$, $Br^-$. Table 2.5

Table 2.5 Summary of main classes of surfactants

| Class | Head group | Main applications |
|---|---|---|
| Anionic | $—CO_2^- Na^+$ | Soaps |
| | $—SO_3^- Na^+$ | Synthetic detergents |
| | $—OSO_3^- Na^+$ | Detergents, personal care products |
| | $—OPO_3^- Na^+$ | Corrosion inhibitors, emulsifiers |
| | $—(OCH_2CH_2)_n—OSO_3^- Na^+$ | Liquid detergents, toiletries, emulsifiers |
| Cationic | $—N(CH_3)_3^+ Cl^-$ | Bitumen emulsions |
| |  | Bactericides, antistatic agents |
| | $—N(CH_3)_2^+ Cl^-$ | Fabric and hair conditioners |
| Zwitterionic | $—\overset{+}{N}(CH_3)_2—CH_2—CO_2^-$ | |
| | $—\overset{+}{N}(CH_3)_2—CH_2—SO_3^-$ | Shampoos, cosmetics |
| Semi-polar | $—(CH_3)_2N \rightarrow O$ | Foam enhancers |
| Non-ionic | $—(OCH_2CH_2)_nOH$ | Detergents, emulsifiers |

Types of Surfactants

1. Anionic surfactants. These include the traditional soaps ($-CO_2^-$) and the early synthetic detergent, the sulphonates ($-SO_3^-$) and the sulphates ($-OSO_3^-$). These still entire feature extensively in cleaning formulation. The major advantage of the sulphonates and sulphates over the carboxylates is their greater tolerance of divalent metal ion hard water.

2. Cationic Surfactants. These are usually quaternary ammonium, imidazolinum or alkyl pyridinium compounds. The positive charge on the head group gives the surfactant a strong substantivity on negatively charged fibbers, such as cotton and hair, and they are therefore used as fabric and hair conditioners.

3. Zwitterionic Surfactants (often referred to as amphoteric). These are used in the form of betaines ($-N^+(CH_3)_2CH_2CO_2^-$) or sulphobataines ($-N^+(CH_3)_2CH_2SO_3^-$). These compounds are milder on the skin than the anionics and have especially low-eye-sting effects, which leads to their anionics and have especially low-eye-sting effects, which leads to their use in toiletries and baby shampoo. Among the naturally occurring surfactants in this class are the important lecithins or phosphatidyl cholines, which have the head group:

$$-O-PO_3^- -CH_2-CH_2-N^+(CH_3)_3$$

4. Non-ionic Surfactants. These are dominated by the ethoxylates, $-(OCH_2CH_2)_nOH$. They are used extensively in low-temperature detergency and as emulsifiers. This class of surfactants also includes several so-called semi-polar compounds such as the amine oxide, sulphoxide andphosphine oxide, although only the amine oxide is commercially important. More recently the variety of non-ionic head groups has been extended to include, for example, pyrrolidones and even sugar. Also to be included in the non-ionic class is the alkanolamides and their ethoxylated derivatives.

### 3.1.3 Comparison of Step-Reaction and Chain-Reaction Polymerization

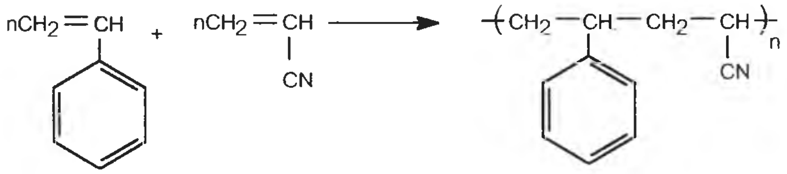
In step-reaction polymerization, molecular weight increases slowly while monomer is consumed rapidly while chain-reaction polymerization; high molecular weights are reached rapidly at low monomer conversions. Furthermore, in chain-reaction processes, initiation, propagation, and termination are all different reactions occurring at different rates and, once termination has occurred, the polymerization cannot proceed further. If, on the other hand, monomer is completely consumed but no termination has taken place, polymerization will continue if more monomer is added. By contrast, in step-reaction polymerization, and once the polymerization reaction ends, the polymer still has reactive end groups. Major differences between the two polymerization processes are summary in Table 2.6

Table 2.6 comparative of step-reaction and chain-reaction polymerization

| Step reaction | Chain reaction |
|---|---|
| Growth occurs throughout matrix by reaction between monomers, oligomers and polymers. | Growth occurs by successive addition of monomer units to limited number of growing chains. |
| Average degree of polymerization low to moderate | Degree of polymerization can be very high. |
| Monomer consumed rapidly while molecular weight increases slowly. | Monomer consumed relatively slowly, but molecular weight increases rapidly. |
| No initiator needed; same reaction mechanism throughout. | Initiation and propagation mechanisms different. |
| No termination step; end groups still reactive | Usually chain-terminating step involved. |
| Polymerization rate decreases steadily as functional groups consumed. | Polymerization rate increases initially as initiators units generated; remains relatively constant until monomer depleted. |

## 2.2 Copolymerization

A copolymer is a polymer made from two or more different monomer. For example, if styrene and acrylonitrile are allowed to polymerize in the same reaction vessel, a copolymer will be formed which contains both styrene and acrylonitrile residues.



Many commercial synthetic polymers are copolymers. It should be noted that the sequence of monomer units along a copolymer chain could vary according to the method and mechanism of synthesis. Four different types of sequencing arrangements are common found.

1. Random copolymers. In random copolymers, no definite sequence of monomer unit exists. A copolymer of monomers A and B might be depicted by the arrangement shown in figure below.

-A-B-B-B-A-A-B-A-A-A-A-B-A-B-B-B-

Random Copolymers are often formed when olefin-type monomers copolymerize by free-radical-type process. The properties of random copolymers are usually quite different from those of the related homopolymers.

2. Alternative copolymers. As the name regular copolymers contains a regular alternating sequence of two monomer unit

-A-B-A-B-A-B-A-B-

Olefin polymerizations that take place through ionic-type mechanism can yield copolymers of this type. Again, the properties of the copolymer usually differ markedly from those of the two related homopolymer.

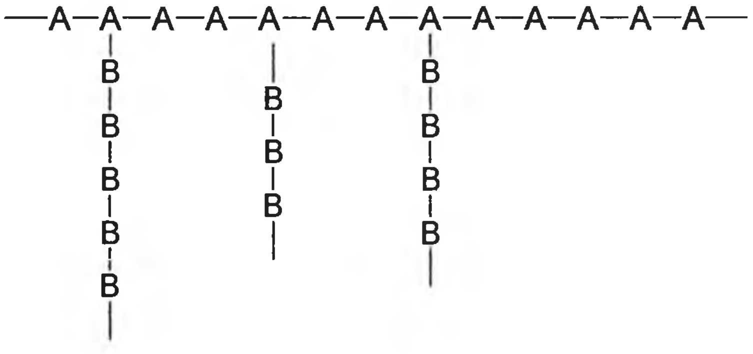
3. Block copolymers contain a block of on monomer connected to a block of another.

-A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-

Block copolymers are usually formed by ionic polymerization process unlike other copolymers; they retrain many of the physical characteristics of the two homopolymer.

4. Graft Copolymer

A graft copolymer usually prepared by linking together two different polymers. For example, a homopolymer derived from monomer A may be induced to react with a homopolymer derived from monomer B to yield graft copolymer shown in figure below. Graft polymers of this type can be often be prepared by gamma or X-irradiation of a mixture of the two homopolymers, or even by mechanical blending of the two homopolymers. Alternatively, a graft copolymer may be prepared by the polymerization of monomer B from initiation sites along the chain of polymer A. Graft copolymers often display properties that are related to these of the homopolymers.



In this topic, the Cellulosic block and graft copolymer would be emphasized.

Vinyl Graft Copolymerization onto Cellousic Fiber

The chemical structure of cellulose can be modified in several ways:

a) By substitution of the cellulose hydroxyls where by the cellulose molecules are altered through introducing side groups, usually by an etherification or by an esterification reaction. The effect of this is to eliminate or at least to reduce some of the outstanding drawbacks of the cellulose, such as flammability susceptibility to rot and mildew, swell ability, etc., and is dependent on the type and extent of the reaction as well as on the nature of the substituent groups.

b) By reacting cellulose with bi-or polyfunctional compounds, which results in the production of cross-links or resinification products in the cellulose, thereby stabilizing its structure such treatments impart crease resistance, shrink resistance, and a number of other properties to the cellulose.

c) By preparing a branched cellulose or what is called a graft copolymer of cellulose, a process in which attempts have been made to combine synthetic polymers with cellulose to produce material with the best properties of both. This process is known as grafting, usually done by modifying the cellulose molecules through creation of branches of synthetic polymers that confer certain desirable properties on the cellulose without destroying its intrinsic properties.

The amount of grafted monomers is usually taken as the increase in weight after solvent-extraction of homopolymer and drying. The percent grafting is defined as the ratio of the increase in weight to the initial cellulose weight as follow.

$$\%\ \text{Grafting} = \left[\frac{\text{Final cellulose weight} - \text{Initial cellulose weight}}{\text{Initial cellulose weight}}\right] \times 100$$

The efficiency of grafting is defined as the ratio of the amount of grafted monomer to that of polymerized monomer.

$$\text{Efficiency of Grafting} = \left[\frac{\text{Final cellulose weight} - \text{Initial cellulose weight}}{\text{Total polymer weight after reaction} - \text{Initial Cellulose weight}}\right] \times 100$$

During synthesis of cellulosic graft copolymers, block copolymers may form if the initiating centers are formed at the end of cellulose molecules or at broken chain ends of the cellulose. The block and graft copolymers to be considered here are defined by schematic structure shown in Figure 2.6. (3) The block copolymer is composed of a cellulose chain to which synthetic polymer segments are chemically linked to form a linear molecule. It is believed that though block copolymers of cellulose would usually be expected to resemble the schematic structure A, schematic structure B cannot be ruled out. The graft copolymer is comprised of a linear backbone polymer, i.e., cellulose, containing branches or "graft" of the synthetic polymer, C. These branches may vary considerably in length depending on particular requirements and copolymerization conditions.

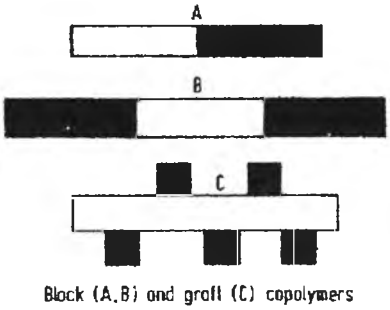


Figure 2.6 Schematic representation of block and graft copolymer (white and black segments represent the cellulose backbone and the synthetic polymer, respectively) (8)

The example for grafting of polyacrylonitrile on Cellulosic material shown in Figure 2.7

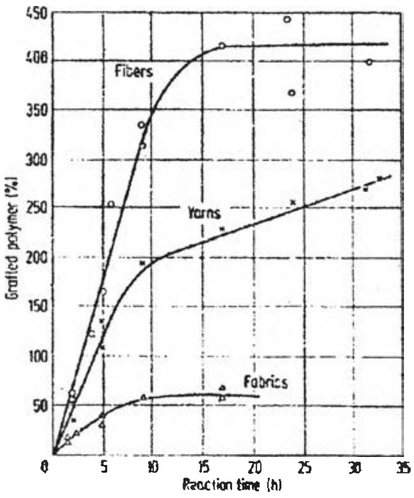
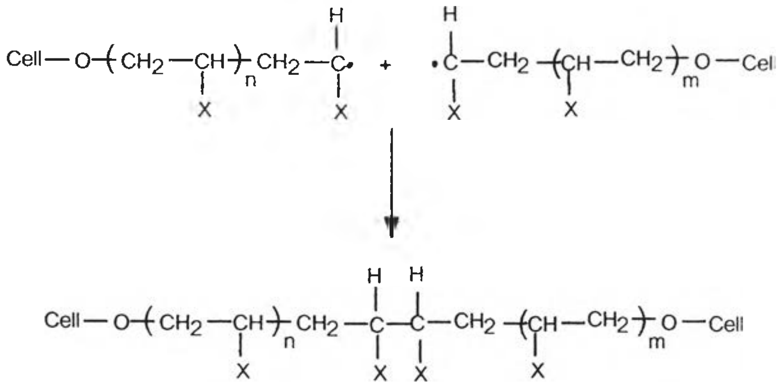


Figure 2.7 Post-irradiation grafting of acrylonitrile in 75% aqueous $ZnCl_2$ to cotton fibers, yarns, and fabrics at about 23°C. Irradiation conditions dry and in nitrogen. (8)

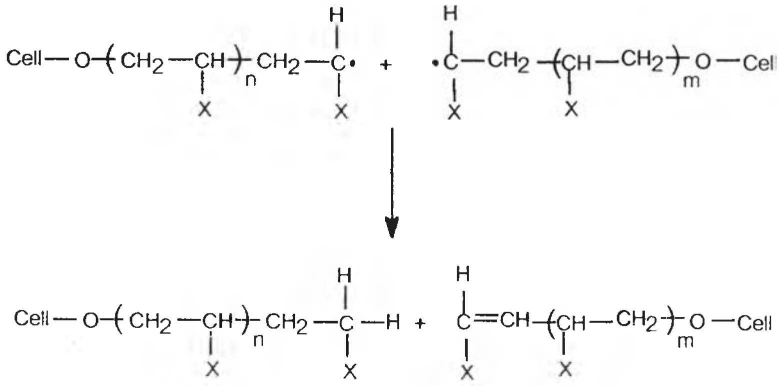
Grafting of a vinyl monomer to cellulose is a typical free radical polymerization reaction, which involves three distinct aspects, namely, initiation, propagation, and termination. Initiation consists of two steps. The first step is to produce free radicals on the cellulose backbone from the initiator. This is generally achieved by abstraction of a hydrogen atom from cellulose molecule.

The second step entails the addition of a monomer molecule to the cellulose free radical, resulting in the formation of a covalent bond between the newly formed branches. Thus, a chain is initiated. This is followed by many subsequent additions of monomer molecules to the initiated chain, thereby propagating the chain.

Termination occurs by combination, where the radicals of two growing polymer chains are coupled:



Or by disproportionation where a hydrogen atom is abstracted by one chain from the other:



Termination may also occur by reaction with impurities, initiator, or activated monomer, or by a chain transfer process.

Free-Radical Initiation

Free radicals capable of initiating graft polymerization may be introduced into cellulose by various chemical methods. In addition to well-established initiators such as peroxides and persulfates, the $Ce^4$ salt system has been widely exploited. Other chemical methods of initiating grafting onto cellulose require chemical modification of the cellulosic substrates so that they can participate in initiation reactions, for example, through the introduction of diazonium groups or unsaturated side chains. Such modifications may be permanent or temporary.

1. Persulfate Initiation

Kolthoff and Miller (7) have shown that when heated, persulfate ions in aqueous solution decompose to produce sulfate ion-radical.

$$S_2O_8^{2-} \longrightarrow 2\ SO_4^{\bullet -}$$

This is a first order reaction. The sulfate radicals may react with water to produce hydroxyl radicals and finally oxygen:

$$SO_4^{\bullet -} + H_2O \longrightarrow HSO_4^- + HO^{\bullet}$$

2. Hydroxyl Radical Initiation

When Fe2+ ions are mixed with $H_2O_2$, $HO^{\bullet}$, radicals are generated. Faber and Weiss (7) have developed the following reaction scheme for the decomposition of hydrogen per oxide in the presence of $Fe^{2+}$ ion:

$$H_2O_2 + Fe^{2+} \longrightarrow HO^- + HO^{\bullet} + Fe^{3+}$$

$$HO^- + Fe^{3+} \longrightarrow HO^- + Fe^{3+}$$

The $HO^{\bullet}$ radicals further decompose $H_2O_2$

$$HO^{\bullet} + H_2O_2 \longrightarrow H_2O + HO_2^{\bullet}$$

$$HO_2^{\bullet}\quad H_2O_2 \longrightarrow HO^{\bullet} + H_2O + O_2^{\bullet}$$

## 2.3 Cellulosic Fiber

Cellulose is the most abundant polymer available today worldwide. Cellulose as a polymer raw material is used for two general purposes: for many centuries it has served mankind as a polymer construction material, mainly in the form of intact wood but also in the form of natural textile fibers like cotton or flax, or in the form of paper and board. On the other hand, cellulosic is a versatile starting material for subsequent chemical conversion, aiming at the production of artificial cellulosed-based treads and film as well as of a variety of stable cellulose derivatives to be used in many areas of industry and domestic life.

### The Molecular Structure

Cellulose is a linear syndiotactic homopolymer composed of D-anhydroglucopyranose unit (AGU), which are linked together by β-(1→ 4)-glycosidic bonds. Taking the dimer cellubiose as the basic unit, cellulose can be considered as an isotactic polymer of cellubiose as the basic unit, cellulose can be considered as an isotactic polymer of cellubiose (Figure2.8). Each of the AGUs possesses hydroxyl groups at C-2, C-3 and C-6 position, capable of undergoing the typical reactions known for primary and secondary alcohol. The vicinal secondary hydroxyl groups represent a typical glycol structure. The hydroxyl groups at both ends of cellulose chain show different behavior. The C-1 end has reducing properties, while the glucose end group with a free C-4 hydroxyl group is non-reducing. The bridging and the ring oxygen atom are predominately involved in intra-and intermolecular interactions mainly hydrogen bond, and in degradation reactions.

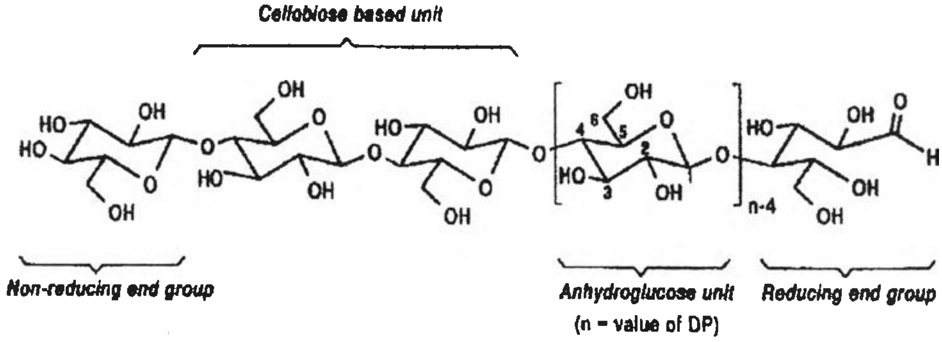


Figure 2.8 Molecular structure of cellulose$^{(9)}$

The monosacharide D-glucose exists in two cyclic forms, α and β. In the β form, all hydroxyl substituents and the hydroxymethyl group are in the equatorial position, whereas in the α form, the hydroxyl at C-1 (the hemiacetal hydroxyl group) is axial.

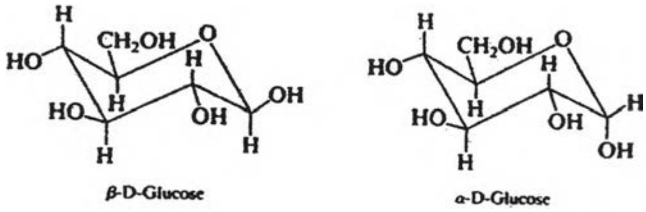

β-D-Glucose α-D-Glucose

Figure 2.9 The monosaccharide D-glucose forms (3)

Supramolecular Structure

Cellulose is highly crystalline material, but it does not form discrete crystals like those of glucose from which it is derived. As already indicated native cellulose fibers consist of crystalline fibrils varying in complexity and length. This fibrillar structure is interspersed with material in which the chain molecules are less well ordered than in a crystal. The same chain molecule may participate in crystalline and less crystalline material along different potions of its length. Native cellulose contains very little genuine non-crystalline material. What used to be regarded as amorphous is generally believed to be the accessible surfaces of some of its crystalline fibrils. The supramolecular structure of cellulose, i.e. the overall arrangement of chain molecules in a fiber, may be considered under two headings: crystalline structure and fine structure. (Fig 2.10)

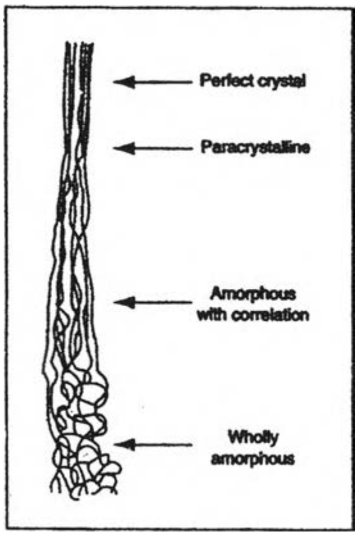


Figure 2.10 Diagram of packing of chain molecules(amorphous to crystalline).

The features of the crystalline structures identified in five forms, but only cellulose I and cellulose II were important in textile processing. Cellulose I is the form in nature, and cellulose II (called “hydrate cellulose”) is thermodynamically stable form produced when cellulose is generated from solution or subjected in the solid state to the process of mercerization. Figure 2.11

The flat ribbons just described pack together into monoclinic unit cell of dimensions approximately a=0.82,b=0.79,c=1.034 nm fiber axis and $\gamma = 97^{\circ}$ in case cellulose I, and a=0.81, b=0.91, c=1.034 nm and $\gamma = 117^{\circ}$ in case of cellulose II. A cross-section of the cell in the ab plane, looking along the fiber axis, is shown in Figure 2.12. Originally Meyer and Misch believe that the center and corner chains were antiparallel to one another, but the latest evidence strongly fervours the parallel arrangement with the centre chains staggered by approximately 0.25c (0.26nm) with respect to the corner chain, as in Figure 2.13. Adjacent chains are held together in a system of hydrogen-bonded sheets in the ac planes as shown in Figure 2.14.

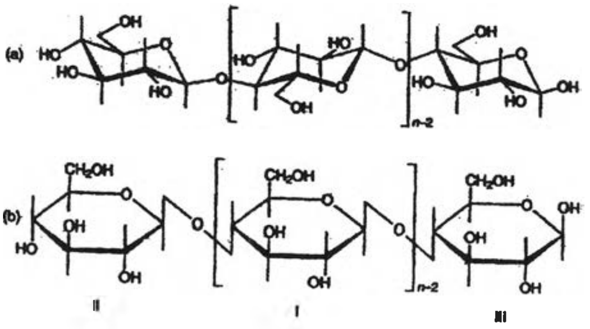


Figure 2.11 Cellulose: (a) fully extended conformational formula: (b) the Haworth projection formula. n= degree of polymerization (DP). (10)

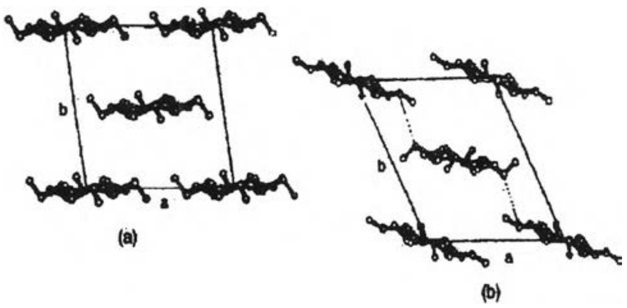


Figure 2.12 Cross-section of unit cell in the ab plane (looking along the fibre axis): (a) cellulose I: (b) cellulose II. (10)

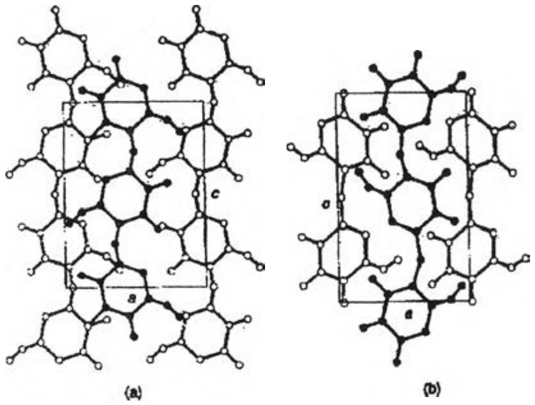


Figure 2.13 Unit cell in the ac plane: (a) parallel-chain model of cellulose I; (b) antiparallel-chain model of cellulose II. (10)

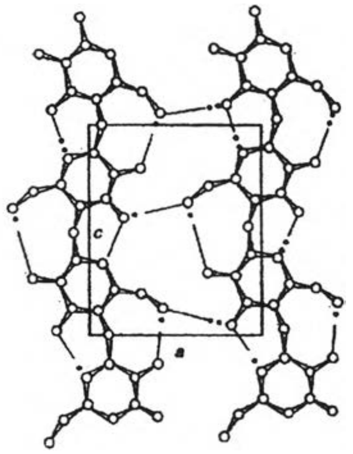


Figure 2.14 Hydrogen bonding in cellulose I. (10)

The fine structure of cellulose is essential for a full understanding of dyeing processes since it is important to know precisely where a dye becomes attached to fiber. It is generally accepted that reagent cannot penetrate the crystalline regions unless they can simultaneously disrupt them.

In the case of cellulosic fibers the idea of fringed micelles, in which crystalline micelles are embedded in as amorphous matrix with individual chain molecules extending through several crystalline and amorphous regions, as Figure 2.15, held sway for long time.

Ideally, the structure of textile fiber should be capable of description in terms of the following five factors: degree of order; degree of localization of order and disorder; the length: ratio of localized units; the sized of localized units; and the degree of orientation of localized units.

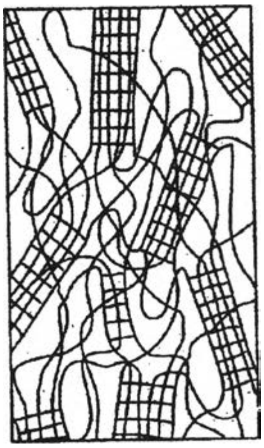


Figure 2.15 Diagram of fine structure in cellulose. (10)

Morphology

The cotton fiber consists of four main parts (12,13). Their morphology illustrated schematically in Fig 2.16. The layers in the cellulose structure are from the outside of the fiber to the inside, cuticle, primary wall, secondary wall, and lumen. The cuticle comprises a very thin outer layer of wax, protein, pectin and mineral matter, is 2.5% of the fiber weight and is amorphous. The primary wall is 2.5% of the fiber weight a crystallinity index of 30%, and is composed of cellulose. The secondary wall constitutes the bulk of the mature fiber and comprises cellulose fibrils arranged spirally around the longitudinal fiber axis laid down in successive layers, the direction of spiral reversing at intervals along the fiber length. The secondary wall is 91.5% of the fiber weight, has a crystallinity index of 70%. The lumen or cavity is composed protoplasmic residues.

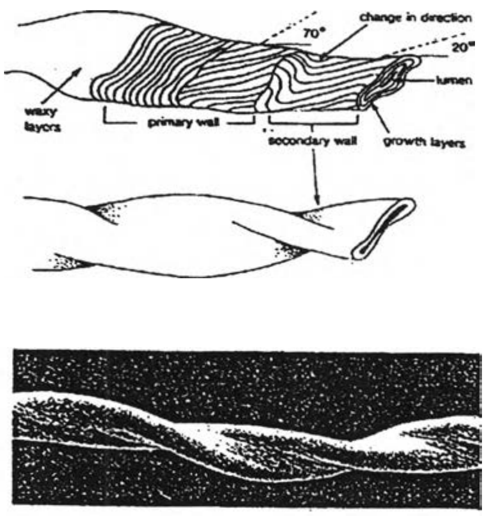


Figure 2.16 The structure of a cotton fiber. (11)

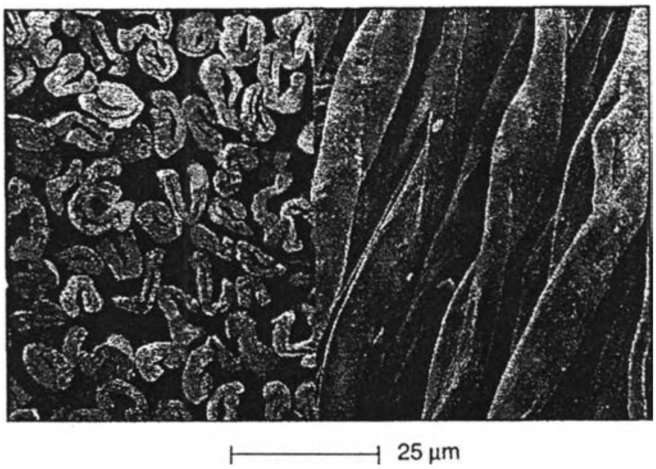


Figure 2.17 Scanning electron micrographs of raw cotton fibres. (10)

### Cotton Properties

Table 2.7 Important physical data of cellulose (9)

| Property | Native fibre | Manmade fibre |
|---|---|---|
| DP (Cuam) | $10^3$-$10^4$ | 250-450 |
| X-ray crystallinity (%) | 50-75 | 25-40 |
| Breaking strength (cN/tex)dry | 26-50 | 14-61 |
| wet | 26-50 | 2-58 |
| Elongation at break (%) dry | 2-10 | 7-30 |
| Wet | 2-11 | 8-40 |
| Elastic modulus (cN/tex) dry | 370-2200 | 265-1950 |
| Spec. resistance at 65% rel. humidity (Ωcm) | $10^5$-$10^9$ | $10^{10}$-$10^{15}$ |
| Dielectric constant ε at 65% rel. humidity | 3-6 (cotton) | 3-7(rayon) |
| Refractive index (parallel) | 1.573-1.595 (cotton) | 1.529-1.571 |
| (perpendicular) | 1.527-1.534 (cotton) | 1.509-1.534 |
| Coefficient of thermal expansion ($K^{1}$) | Ca. $10^{-4}$ | Ca. $10^{-5}$ |
| Thermal decomposition point (°C) | 180-250 | 180-250 |
| Water vapor regain at 65% rel. humidity (%) | 7-8 | 12-14 |
| Water retention value (%) | 50-80 | 70-140 |
| [η]-DP-relation of dissolved cellulose in | | |
| Cuam | $[\eta] = 1.37 \times DP^{0.72}$ | |
| Cuen | $[\eta] = 1.75 \times DP^{0.69}$ | |
| Cadoxen | $[\eta] = 1.67 \times DP^{0.71}$ | |
| FeTNa | $[\eta] = 4.85 \times DP^{0.61}$ | |

Table 2.8 Properties of cotton (14)

| <u>Molecular Structure</u> | Long chain of cellulose |
|---|---|
| Microscopic Features | |
| Length: | 25 to 60 nm. |
| Width: | 12 to 20 μm. |
| Cross-section: | Bean-shaped |
| Color: | Usually a creamy off white color |
| Light reflection: | Low luster, dull appearance |
| Physical Properties | |
| Tensile strength: | 96,700 pound/inch$^2$ |
| Elongation: | 4 to 13 % elongation at break |
| Tenacity (g/cm$^3$) | 1.54 to 1.62 |
| Moisture content: | 8.5% |
| Resiliency: | Low |
| Toughness and stiffness: | High |
| Abrasion resistance: | Fair to good |
| Chemical Properties | |
| Sunlight and heat: | May be heated in the dry state to a temperature of 150 °C without undergoing decomposition but can be damaged by excessive light. |
| Organic solvents: | Resistant to most organic solvents. |
| Effect of bleaches: | Can be bleached without fiber damage. |
| Acids and alkalis: | Highly resistant to alkali. Strong mineral acid causes fiber damage readily and organic acids do a little damage. |
| Dyeability: | Good affinity for a various types of dyes. Dyeable with direct, vat, sulphur and reactive dyes. |

| | |
|---|---|
| Biological Properties | |
| Effects of microorganisms: | Vulnerable to action by bacteria and mould. |
| Effects of insects: | Starched cotton are attacked by silverfish |
| Optical Properties | |
| Axial refraction: | 1.596 |
| Transverse refraction: | 1.534 |
| Double refraction: | 0.062 |
| Electrical and thermal conductivity | Good heat conductor. |
| Flammability behavior | Burns very readily and once ignited, a fabric will carry flame. |

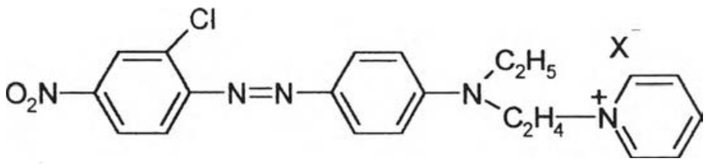
## 2.4 Basic Dyes

Because of the positive charge when these dyes dissolve in water, so this dye class called cationic, or basic dyes. Their brilliance these dyes are used for dyeing acrylic, acid-modified polyamide and polyester fiber.

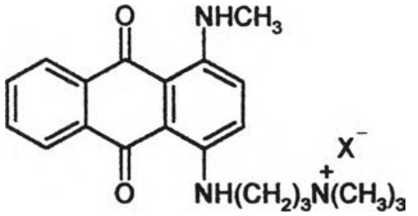
Generally, basic dyes have no affinity for cellulosic fiber the small number of acidic groups and the surface negative potential associated with the immersion of cellulosic fiber in water. For cotton they involved the application of tannin (tannin acid) which could be fixed using a suitable metal salt (tartar emetic, 2 $(K(SbO)C_4H_4O_6))H_2O)$ followed by application of the dye. In this method the tannic acid complex on the fiber serves as a mordant with which the basic dyes can interact.

Basic dyes can be divided in two main types according to their positive charge location:

1) Localized or pendant cationic dyes, in which the positive charge is localized on one atom, usually a nitrogen atom.



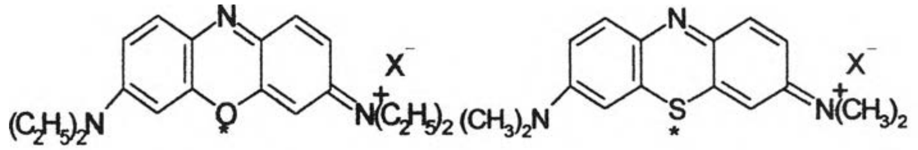
C.I. Basic Red 18 (Azo)



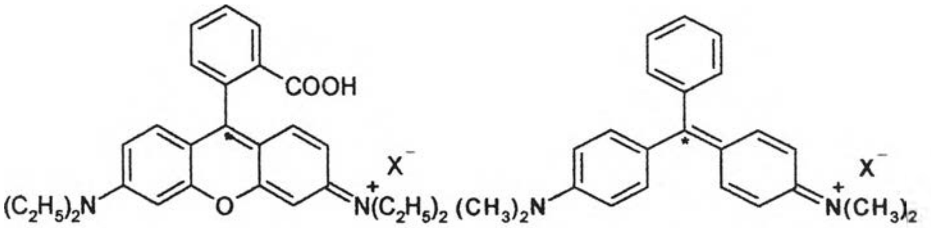
C.I. Basic Blue22 (Anthaquinone)

Figure 2.18 Examples of localized basic dye (17)

2) Delocalized cationic dyes, in which the positive charge Is delocalized over the entire dye molecule (alternate locations for the positive charges are shown with asterisks(*) )



C.I. Basic Blue 3 (Oxazine) C.I. Basic Blue 9 (Triazine)



C.I. Basic Violet 10 (Xanthene)

C.I. Basic Green 4 (Triphenyl methane)

Figure 2.19 Examples of delocalized basic dyes (17)

It is basic dyes with delocalized charges, which are responsible for the intense colors associated with the basic dyes. Most localized basic dyes are azo or anthaquinone types, often with a localized quaternary ammonium group isolated from the chromophoric grouping by a saturated aliphatic chain. Such the dyes often exhibit better light fastness than the traditional delocalized types. (18)

**Dyeing Mechanism**

The dyeing mechanism for acrylic fiber takes place by the successive steps of sorption at the fiber surfaces, diffusion into the fiber and fixation or retention of the dye by the fiber.

1) Dye Sorption: Sorption of basic dye cations at fiber surfaces can be expected to occur at a particularly rapid pace. This is due to the surface negative potential associated with the immersion of all fibers in water and sometimes referred to as the zeta potential. Consequently the intrinsic coulombic attraction of the dye cations for the anions of the fiber substrate is enhanced. Saturation of the immediate fiber. Surface takes place very rapidly unless there is insufficient dye in the bath.

2) Diffusion from the Surface: Below the glass transition temperature ($T_g$) –i.e., below 0-80° C (160-175 F) – dye diffusion in the fiber is slow due largely to the lack of mobility in the polymer segments but also due to strong attraction between the fiber anions and the dye cations.

With the exception of dyeing using very small percentages of dye, the diffusion stage takes place when a layer of color saturates the fiber surfaces and maintains a constant by concentration. Therefore the early rate of dyeing is practically independent of the concentration of dye remaining in the dyebath. This means the rate is independent of the liquor ratio. Once above the glass transition temperature, the rate of dyeing increases extremely rapidly. The rate of dyeing acrylic doubles every 2.5-3° C (4.4-5.5F). This is particularly important since the majority of basic dyes level quite poorly although there are some never dyes with less substantively and generally small molecules, which level much better. If unlevelness does occur, thermoplasticity of the fibers makes it dangerous to attempt leveling at high temperature or by extending the normal dyeing time.

The high wet fastness of basic dyes on acrylic fibers can be attributed to the fact that most washing procedures take place well below the glass transition temperature when the dye is for all practical purposes trapped inside the hydrophobic fiber.

In practical dyeing, during both the surface sorption and dye diffusion phases, it is important that dyes used are compatible; i.e. that they exhaust at the same or very similar rates and that the rates are not too high to preclude level dyeing.

3) Dye Fixation: It is easy to think of basic (cationic) dyeing of acrylic fibers with their anionic charges taking place by means of a glorified ion exchange mechanism. It may be more convenient to think of it this way rather than as another complex ion distribution problem like that for nylon4,5. Certainly the sorption and diffusion processes are significantly different from those of acid dyes on nylon and overdyeing seems to be less prevalent.

The concentrations of anionic groups in acrylic fiber are generally quite low and are largely made up of permanently ionic groups, $-SO_3^-$ and $-OSO_3^-$, with no equivalent fiber cation groups. These anionic groups do not change in concentration with changing pH in the dyebath range. Only those fibers containing carboxylic acid groups have concentrations of anions, which are pH dependent, increasing with increasing pH.

Different acrylic and modacrylic fibers have quite a range of concentrations of available anionic charges, which lead to very different capacities for dyes at fiber saturation. The capacities are rarely exceeded. The fiber dyes very rapidly above the glass transition temperate and the possibility of unlevelness is of great concern.

## 2.5 Preview Research Works on an Attempt to Modify Cellulose to Improve Its Dyeability with Basic Dyes

### 2.5.1 Physico-Chemical and Chemical Methods to Improve Basic Dyeability of Cotton

M.ueda *et al.* (19,20) introduced UV-irradiation onto cotton substrate. The UV-irradiated cotton revealed that the substrate was photo-oxidized FTIR and XPS analyses suggested that aldehyde group may have been formed at the surface of the irradiated cotton substrate.

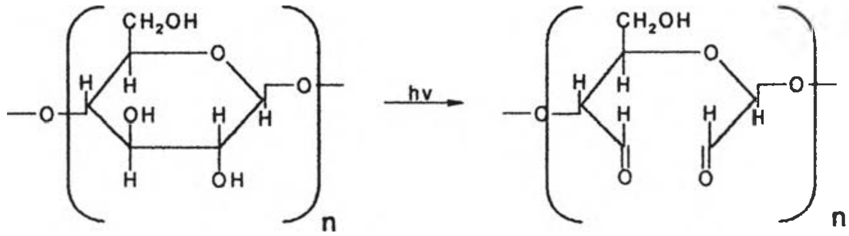


Figure 2.20 Supposed reaction scheme of the photo-oxidation conversion of the cellulosic substrate by the UV irradiation (20)

Carboxylic acid occurred by oxidation of aldehyde. Finally, carboxylic acid groups formed at the surface of the substrate. For this reason, the dye ability of the UV-irradiation cotton with cationic dye was enhanced with the dye ability of treated cotton decreased for anionic (i.e., direct, reactive) dye Figure 2.21. Because of breaking chain of cellulose so tear strength of the treated cotton dropped significantly with increasing time of exposure to UV light.

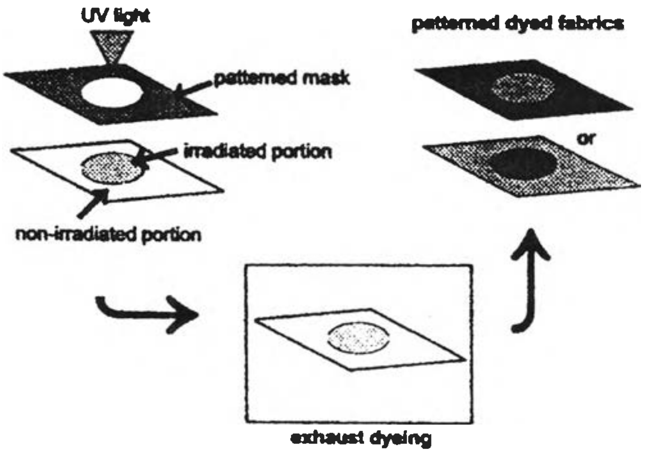


Figure 2.21 Schematic illustration of novel patterned dyeing method.

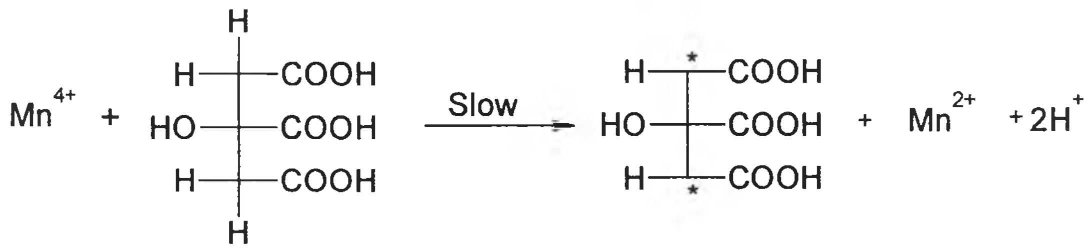
A. Hibash et al. (21) studied grafting and dyeing using a potassium permanganate/citric acid imitation system to induced polymerization of acrylonitrile onto loomstate cotton fabric. The one-step polymerization/dyeing process was carried out under different conditions. (concentration of initiator, duration, temperature of polymerization, monomer concentration, pH, liquor ratio )

**Possible Grafting/Dyeing Mechanism**

When loomstate cotton fabric was treated with potassium permanganate, a substantial amount of manganese dioxide was deposited on the fabric. In presence of citric acid, it is believed that carboxyl radical are formed as a result of the action of citric acid through reduction of Mn (IV) to either Mn (III) or Mn (II) (Scheme 2.2). Once these free radical species($R^\bullet$) are created, they produce reactive sites located along the cellulose or the dye molecule (Scheme 2.3). Cellulose macro radicals or dye radical may also be formed by direct attack of Mn (IV) or Mn (III) ions on the cellulose or dye molecule via abstraction of a hydrogen atom (Scheme 2.4).

In the presence of acrylonitrile monomer, the reactive sites (formed according to Scheme 3 and 4) were added to the double bond of acrylonitrile, resulting in a covalent bond between the monomer and the cellulose, accompanied by the creation of a free radical on the monomer, i.e. chain initiation as shown in Scheme 2.5. Subsequent addition of monomer molecules lead to propagation of grafting as suggested by Scheme 2.6.

During polymerization the dye radical may combine with the cellulose macro radical of growing grafted chain radical, becoming chemically bound into the cellulose backbone. It is also likely that the dye radical can initiate homopolymerization of acrylonitrile (Scheme 2.7) and become an integral part of the homopolymer. Once the latter is intimately associated with the cellulose, it will contribute to the colour strength of the fabric.



Scheme 2.1

$$Mn^{3+} + H_2O \longrightarrow Mn^{2+} + H^{+} + HO^{\bullet}$$
$$Mn^{4+} + H_2O \longrightarrow Mn^{3+} + H^{+} + HO^{\bullet}$$

Scheme 2.2

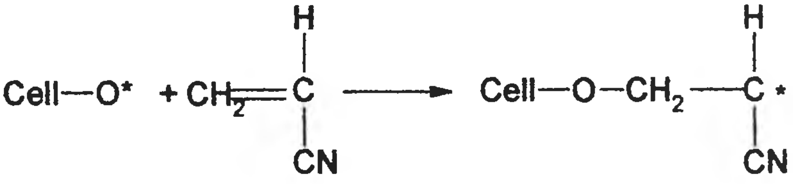
$$\text{Cell—OH} + R^{*} \longrightarrow \text{Cell—O}^{*} + \text{R—H}$$

$$\text{dye—XH} + R^{*} \longrightarrow \text{dye—x}^{*} + \text{R—H}$$

Scheme 2.3

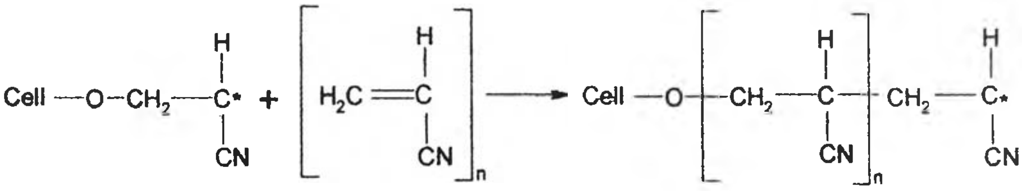
$$\text{Cell—OH} + Mn^{4+} \longrightarrow Mn^{3+} + H^{+} + \text{Cell—O}^{*}$$
$$\text{Cell—OH} + Mn^{3+} \longrightarrow Mn^{2+} + H^{+} + \text{Cell—O}^{*}$$
$$\text{D—X—H} + Mn^{4+} \longrightarrow \text{D—X}^{*} + Mn^{3+} + H^{+}$$
$$\text{D—X—H} + Mn^{3+} \longrightarrow \text{D—X}^{*} + Mn^{2+} + H^{+}$$

Scheme 2.4



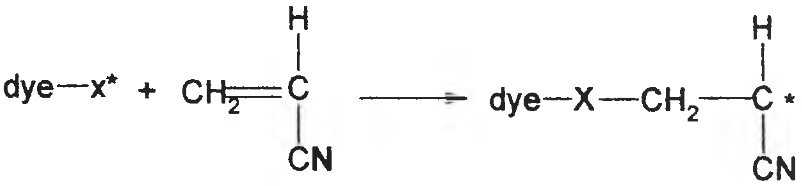
$$\text{Cell—O}^{*} + CH_2{=}\overset{\displaystyle H}{\underset{\displaystyle CN}{C}} \longrightarrow \text{Cell—O—}CH_2\text{—}\overset{\displaystyle H}{\underset{\displaystyle CN}{C}}{}^{*}$$

Scheme2.5



$$\text{Cell—O—}CH_2\text{—}\overset{\displaystyle H}{\underset{\displaystyle CN}{C}}{}^{\bullet} + \left[ H_2C{=}\overset{\displaystyle H}{\underset{\displaystyle CN}{C}} \right]_n \longrightarrow \text{Cell—O}\left[ CH_2\text{—}\overset{\displaystyle H}{\underset{\displaystyle CN}{C}} \right]_n CH_2\text{—}\overset{\displaystyle H}{\underset{\displaystyle CN}{C}}{}^{\bullet}$$

Scheme 2.6



$$\text{dye—x}^{*} + CH_2{=}\overset{\displaystyle H}{\underset{\displaystyle CN}{C}} \longrightarrow \text{dye—X—}CH_2\text{—}\overset{\displaystyle H}{\underset{\displaystyle CN}{C}}{}^{*}$$

Scheme 2.7

Scheme 2.1-2.7 possible grafting/dyeing mechanism (21)

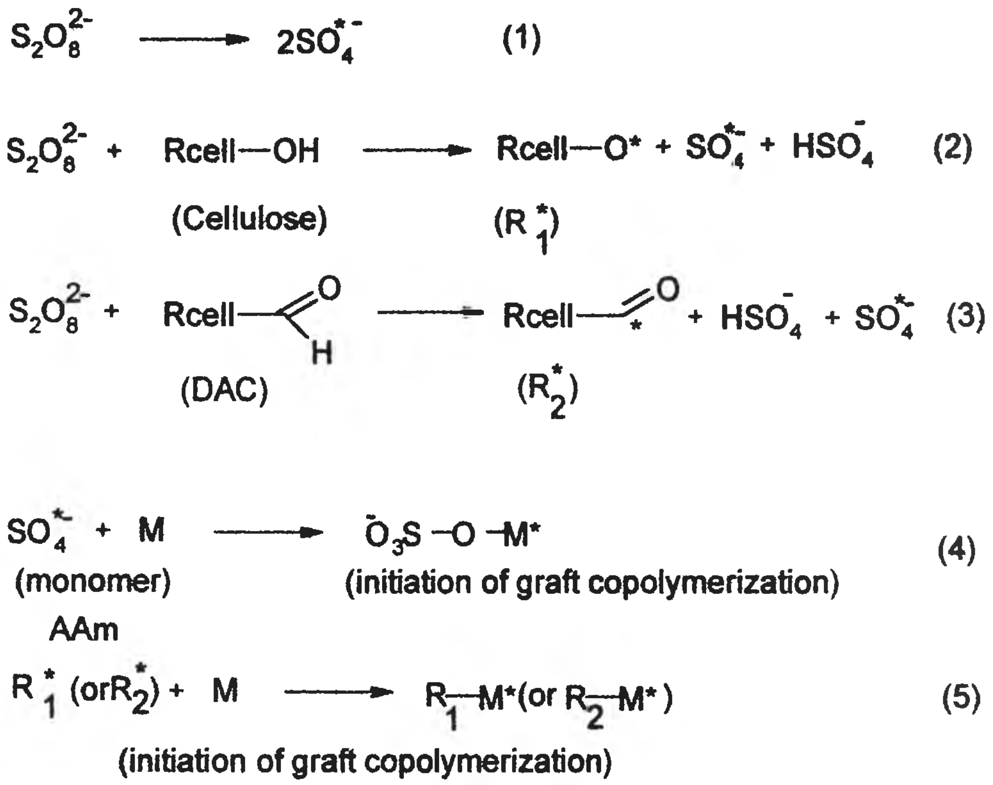
The presence of either of the dyes used in this research in a polymerization system containing cotton fabric, acrylonitrile, potassium permanganate/citric acid and water seem to provide an effective means for concurrent grafting and dyeing. Formulation consisting of 0.05 g/l potassium permanganate, 0.1 g/l citric acid. 50% acrylonitrile, 1% dye and 2 g/l wetting agent is considered appropriate for concurrent grafting and dyeing, provided that treatment is carried out for 60 min at $90^{\circ}$ C and pH3.

The graft yield and colour strength exhibit similar trends when their dependence on factors affecting the grafting/dyeing operation were considered. Meanwhile fabric sample concurrently grafted and dyed displayed much greater colour strength than samples that were merely dyed. Losses in colour strength after washing of the graft/dyed samples were also much lower than with the dyed samples.

Dyeing seems to occur during the polymerization process and to proceed according to a free radical mechanism. Chemical bonds can be formed by coupling of dye free radical with a cellulose macroradical, as well as via coupling of the growing polyacrylonitrile chain with the cellulose macroradical. In combination with this are the homopolyacrylonitrile-containing dye molecules that are so intimately associated with the cotton that they cannot be removed during washing.

A different situation is encountered when the cotton fabric is subjected to dyeing under conventional conditions. The dye molecules here are essentially held in the cotton structure by only physical forces (hydrogen bonding and Van der Waals forces).

P.Ghosh*, D.Der, and A.K. Samanta (22) researched graft copolymerization of acrylamide on cotton (dialdehyde cellulose, DAC) fibers and fabric in a limited aqueous system using $K_2S_2O_8$ as the initiator. As seen in Scheme 2.8



Scheme 2.8 The mechanism of graft copolymerization of acrylamide on cotton.

Reaction (1) describes the primary radical generate step, reaction (4) shows initiation of homopolymerization of acrylamide reaction (2) and (3) show the possible means of radical generation on the cellulose and dialdehyde cellulose (DAC) chain by a redox mechanism, the cellulose/DAC chain units activating the decomposition of $S_2O_8^{2-}$ to radicals, and reaction (5) shows major means of polyacrylamide grafting on cellulose /DAC chain segments. Between reaction (2) and (3), the latter is faster in view of higher reducing power of the aldehyde groups than the hydroxyl groups.

Finally, they concluded that controlled low degrees (9-10%) of grafting of polyacrylamide on cotton fabric of low degree of oxidation (dialdehyde cellulose, DAC, copper number 4.0) induced by $K_2S_2O_8$ in limited aqueous system at $60^{\circ}C$ results in improved property parameters for the fabric, viz. dyeability with reactive and acid dyes, tenacity, and moisture regain. Concomitantly, the fabric gains much in stiffness (bending length) and modulus. Such modification enhances the prospect of the use of relevant grafted fabrics in such applications as stiff and durable lining for apparels, tarpaulins, canvas, betting and soft luggage.

### 2.5.2 The Researches Concern with This Research

Microemulsions are optically isotropic, transparent or translucent, and thermodynamically stable dispersions of two immiscible liquids stabilized by a combination of surfactant and long-chain alcohol or amines. (23)

Microemulsions are transparent, homogenous, isotropic, thermodynamically stable systems formed commonly by add in the couple surfactant-cosurfactant, usually the latter being a $C_4$-$C_5$ alcohol. Their particles are one to two orders of magnitude smaller (100$^{\circ}$ A), than emulsion. (24) The microemulsion stability is therefore due also to entropic factors and to the triple role of the cosurfactant, (I) obtainment of very low interface tension, (ii) availability of many different structures, (iii) formation of flexible interfacial films.

F.J. Carrion (25) investigated the influence of the temperature on the sorption of microemulsionated cationic softeners on cotton. If the softener is in microemulsion form, then it penetrates readily into the interior of the fabric structure, giving the better results than can sometimes be achieved with the larger particle size of more conventional products.

Recent study of the emulsion polymerization of butyl methacrylate initiated by 2.2'-azobisisobutyronitrile (AIBN) has shown that in this system part of the AIBN is transferred from the oil to the aqueous phase(26). This fact can be used for initiating the polymerization of the system consisting of the aqueous phase contain a water-soluble monomer, and the oil phase form by an organic solvent containing the initiator. If transfer of the monomer to the oil phase is improbable, then the initiation may occur only in; the aqueous phase, namely by radicals formed via thermal decomposition of the transferred initiator in the aqueous. Such a reactive system is a simple model of partitioned polymerization.

Achwat W.B. (27) showed grafting of acidic monomers such as acrylic and methacrylic acids to cellulose significantly improved its affinity to basic dyes. For example, the introduction of small amounts of carbonyl groups (1.8-2% on the weight of material) by grafting cellulose with acrylic acid considerably improved the absorption of basic dyes.

## 2.6 Concepts of an Alternative Method for Modifying Cellulose

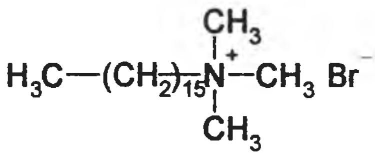
In the several decades, researchers tried to modify cellulosic fibers for their requirements. Generally, the modification methods may be into classified two methods:

1) physico-chemical method (1)

2) chemical method, such as graft copolymerization. (8)

The details were discussed earlier.

The aim of this project was to modify cotton to improve its dyeability with basic dyes, which have high molar absorptivity and offer an ease of dyeing process compared to reactive dyeing. An attention was paid to an exploitation of the oil-in-water microemulsion technique to assist the in-situ polymerization of methacrylic acid inside the interior of cellulose fiber. The interested microemulsion system was based on CTAB-benzene/propanol-water system, which exhibited cationic characteristic. It was believed that positively charged microemulsion droplets containing water insoluble initiator could diffuse easily into the interior of cellulose by electrostatic interaction between negatively charged fiber surface and the positively charged microemulsion. Consequently, the water insoluble initiator was introduced into the amorphous region of cellulose since the microemulsion particles was very small (less than 100 °A). The schematic of oil-in-water microemulsion droplet containing water insoluble initiator (2,2'-azobisisobutyronitrile, AIBN) could be illustrated as shown is Figure 2.22



$$H_3C-(CH_2)_{15}-\underset{CH_3}{\overset{CH_3}{N^+}}-CH_3\ Br^-$$

Figure 2.22 Structure of Cetyltrimethylammonium Bromide

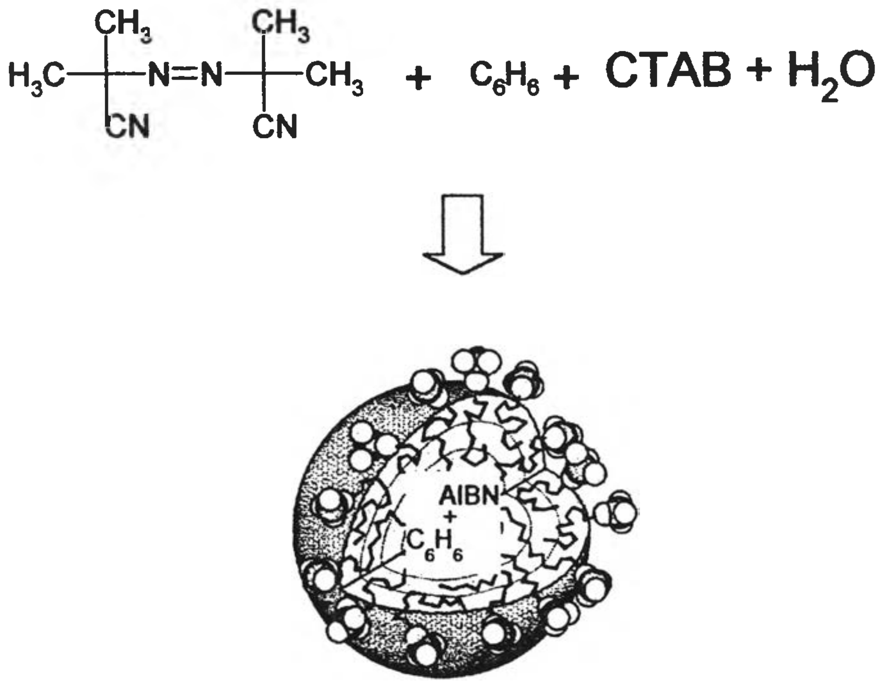


Figure 2.23 microemulsion micelles consisted of CTAB, AIBN and Benzene

When immersing cotton into the above microemulsion solution, it was anticipated that microemulsion droplets diffused into the amorphous regions, as shown in Figure 2.24

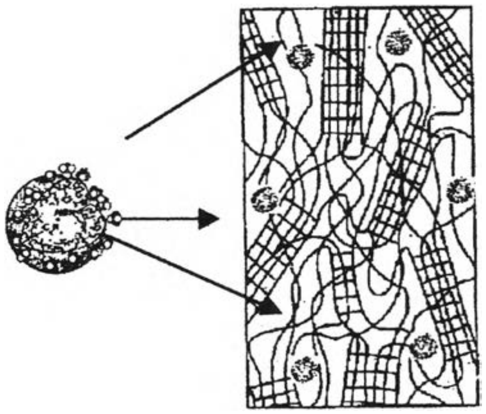
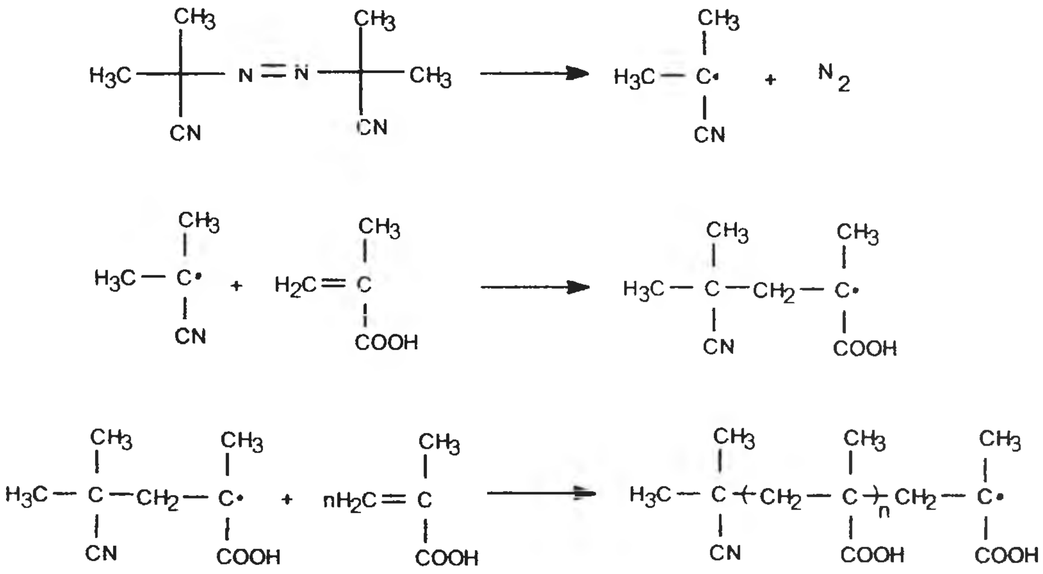


Figure 2.24 The diffusion of microemulsion into the amorphous region of cellulose

Then miscroemulsion treated cotton fabric was immersed into the methacrylic acid solution and followed by heating. The water-insoluble initiator would decompose to radicals. The radicals would transfer from oil phase to aqueous phase (26), so initiation and propagation occurred, as Scheme 2.9



Scheme 2.9 shows initiation and propagation of polymerization of methacrylic acid

Finally, the produced polymethacrylic acid was entangled inside the cellulosic chain. The properties of modified cellulose including basic dyeability and moisture regain were evaluated. The percentage of dye exhaustion and the degree of dye fixation would be determined spectrophotometrically. The percentages of polymer add-on, moisture regain, fastness properties including washing fastness and light fastness, and cross-section of the treated cotton dyed basic dye would be discussed.
]